Thermophysical Properties of Quinoxaline Derivatives and Their Binary Mixtures with Organic Solvents at Various Temperatures

G RAPHAEL

orcid.org/0000-0002-4915-2991

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Promoters: Prof Indra Bahadur
Prof Eno E. Ebenso

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Student number: 25234633

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DECLARATION

I hereby declare that the thesis entitled "THERMOPHYSICAL PROPERTIES OF QUINOXALINE DERIVATIVES AND THEIR BINARY MIXTURES WITH ORGANIC SOLVENTS AT VARIOUS TEMPERATURES" submitted to the Department of Chemistry, North-West University, for the fulfilment of the requirements of the degree of Doctor of Philosophy (Ph.D) in Chemistry is a faithful record of original research work carried out by me under the guidance and supervision of Prof Indra Bahadur and Prof Eno. E. Ebenso. No part of this work has been submitted by any other researcher or students in any tertiary institution or University. Sources of my information have been properly acknowledged in the reference pages.

Signature..R. Gnanapragasam.....Date.....02/05/2018

Gnanapragasam Raphael

Signature..... Date.....

Prof Indra Bahadur

Signature..... Date.....

Prof Eno. E. Ebenso

DEDICATION

Dedicated to:

- Almighty God
- My late parents: Antony Raphael & Jayamary Raphael
- My late brother: Vanathayan Raphael
- My wife: Saroja Gnanapragasam
- My sons: Rufus Prakash Gnanapragasam & Surya Prakash Gnanapragasam

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ABSTRACT

Quinoxaline and its derivatives are an important class of N-heterocyclic compounds. They are very much useful in pharmacological industry since they exhibit biological activities such as antibacterial, antifungal, anticancer, antimalarial, anti HIV, antidiabatic etc. Many quinoxaline derivatives have wide application as dyes, electroluminescent materials, organic semiconductors, cavitands, chemically controllable switches and DNA cleaving agents. To enhance the application of quinoxaline, there is need for interaction study with organic solvents at different temperatures and concentration. Therefore, the present study examines the effect of temperature and concentration on interactions of methyl acetate with the aqueous or alcoholic solution of quinoxaline derivatives using volumetric and acoustic properties. New data on thermophysical properties such as densities (ρ), and sound velocities (u), of methyl acetate in aqueous or alcoholic solution of twelve quinoxaline derivatives namely: **Group I,** aqueous solutions of (N-{-3-[1-methanesulfonyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl] phenyl} methane sulfonamide MQDPMS, N-{-2-[1-acetyl-5-(quinoxalin-5-yl)-4, 5-dihydropyrazol-3-yl] phenyl} methane sulfonamide AQDPMS, N-{-2-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihdro-1H-pyrazol-3-yl] phenyl} methane sulfonamide 2PQDPMS, N-{-3-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-3-yl] phenyl} methane sulfonamide 3PQDPMS. **Group II & III,** alcoholic solutions (because they are not soluble in water); 1-[3-(2H-1,3-benzodioxal-5-yl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one BQDB, 1-[3-(3-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]propan-1-one 3MQDP, 1-[3-phenyl-5-quinoxalin-6-yl-4,5-dihydropyrazol-1-yl]butan-1-one 3PQDB, 1-(3-(4-chlorophenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl) propan-1-one 4CQDPP, 2-phenyl-1-[[3-phenyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]ethanone 2PQDE, 1-(3-(4-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl)butan-1-one 4MQDPB, 2-ethyl-1-(5-(quinoxalin-6-yl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)butan-1-one 2EQDPB and 1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-

yl]butan-1-one, 4MQDB, have been measured at (293.15, 298.15, 303.15, 308.15) K and at atmospheric pressure. These data have been used to calculate the derived properties such as apparent molar volume (V_φ), and apparent molar adiabatic compressibility (K_φ). The limiting apparent molar volumes (V_φ^0), limiting apparent molar volumes of transfer (ΔV_φ^0), limiting apparent molar adiabatic compressibility (K_φ^0), and limiting apparent molar adiabatic compressibility (ΔK_φ^0), of transfer have been evaluated by fitting Redlich-Mayer type equation and reasonable correlations were achieved. These results have been interpreted in terms of effect of temperature and concentration on interactions such as solute-solute, solute-solvent and solvent-solvent in the mixtures. Furthermore, the limiting apparent molar expansibility, (E_φ^0), and the Hepler's constant $\left(\partial^2 V_\varphi^0 \Big/ \partial T^2\right)_P$ values, have been evaluated to support the conclusions drawn from volumetric and acoustic studies. These results have been interpreted in terms of effect of temperature, concentration as well as structural variation of quinoxaline derivatives on interactions such as solute–solute, solute–solvent and solvent–solvent which exist in the mixtures.

The results from these studies can be utilized in flow assurance and oil recovery, effective design of separation processes, solvent selection and emission, estimation of the distribution of chemicals in various ecosystems.

Keywords: Quinoxaline, Density, Sound velocity, Methyl acetate, Apparent molar volume, Apparent molar adiabatic compressibility, Redlich-Mayer type equation.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOTATIONS

ρ	Density.
V_m^E	Binary excess molar volume.
V_{min}^E	Minimum binary excess molar volume.
z	Mole fractions ratio between the 3rd and 1s component of the ternary system.
T	Temperature.
K	Kelvin.
x_1	Mole fraction of the 1st component.
x_2	Mole fraction of the 2nd component.
σ_v	Standard deviation of apparent molar volume.
σ_κ	Standard deviation of apparent molar isentropic compressibility.
M	Molar mass.
A_i	Polynomial coefficient.
N	Polynomial degree.
n	Number of experimental point.
k	Number of coefficients used in the Redlich –Kister equation.
V_ϕ	Apparent molar volume.
V_ϕ^0	Apparent molar volume at infinite dilution.
E_ϕ^0	Infinite dilution apparent molar expansibility.
S_v	Empirical parameter for apparent molar volume.
B_v	Empirical parameter for apparent molar volume.
u	Sound velocity.
κ_s	Isentropic compressibility of mixture.
κ_{s0}	Isentropic compressibility of pure solvent.

κ_ϕ	Apparent molar adiabatic compressibility.
κ_ϕ^0	Apparent molar adiabatic compressibility at infinite dilution.
S_k	Empirical parameter for apparent adiabatic compressibility.
B_k	Empirical parameter for apparent adiabatic compressibility.
m	Molality.
mp	Melting point.
mmol	Milli mole.
TLC	Thin layer chromatography.
IR	Infrared spectra.
NMR	Nuclear magnetic resonance.
FTIR	Fourier transform ifrared spectroscopy.
UV-Vis	Ultraviolet visible spectra.
MQDPMS	(N-{-3-[1-methanesulfonyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl] phenyl} methane sulfonamide.
AQDPMS	N-{-2-[1-acetyl-5-(quinoxalin-5-yl)-4, 5-dihydropyrazol-3-yl] phenyl} methane sulfonamide.
2PQDPPMS	N-{-2-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihdro-1H-pyrazol-3-yl] phenyl} methane sulfonamide.
3PQDPPMS	N-{-3-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-3-yl] phenyl} methane sulfonamide.
BQDB	1-[3-(2H-1,3-benzodioxal-5-yl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one.
3MQDP	1-[3-(3-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]propan-1-one.
3PQDB	1-[3-phenyl-5-quinoxalin-6-yl-4,5-dihydropyrazol-1-yl]butan-1-one.

4CQDPP	1-(3-(4-chlorophenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl) propan-1-one.
2PQDE	2-phenyl-1-[3-phenyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]ethanone.
4MQDPB	1-(3-(4-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl)butan-1-one.
2EQDPB	2-ethyl-1-(5-(quinoxalin-6-yl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazoll-1-yl)butan-1-one.
4MQDB	1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one.

CHAPTER 1

INTRODUCTION

1.1 Quinoxaline and its derivatives

Quinoxaline and its derivatives are an important class of heterocyclic compounds, in which N replaces one or more carbon atoms of the naphthalene ring [1, 2]. The approved location for the quinoxaline ring system is shown in **Fig.1.1** [3].

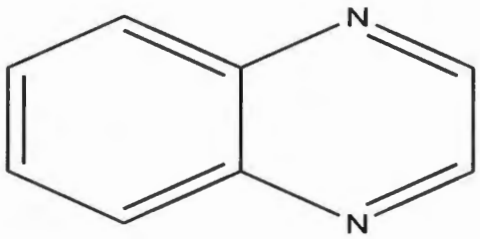


Fig 1.1 Chemical structure of quinoxaline compound.

Quinoxaline is formed by the fusion of two aromatic rings: benzene and pyrazine, because of this reason quinoxaline is also called benzopyrazine and is described as a bioisoster of (quinoline, naphthalene and benzothiophene) [4].

Quinoxalines are mostly synthetic in nature with low melting point (29-30 ºC) solid and basic [5]. The atoms S and N play an important role in the ring since they stabilize ion radical species. The Molecular weight of the quinoxaline is 0.13015 $g.mol^{-1}$, with a molecular formula of $C_8H_6N_2$, and it is a white crystalline powder, at standard conditions (T= 273.15 K and atmospheric pressure of exactly 1 atm (1.01325 × 105 Pa)) [2]. The quinoxaline compounds are very important in the pharmacological industry and have the potential inhibit metal corrosion [5-8], to the preparation of the porphyrins since their structure has chromophores in the natural system, and their utility in the electroluminescent materials [9-11].

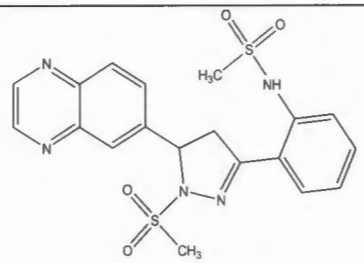
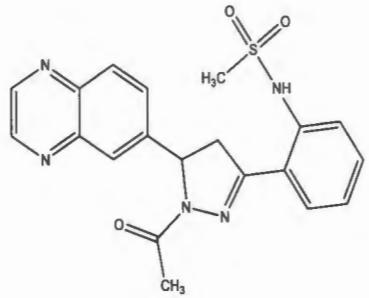
There are very few reported studies in literature on the solubility of quinoxaline and its derivatives [12]. The knowledge of solubility of quinoxaline in methyl acetate at different temperatures is vital in physical stability studies of liquid dosage forms, in processes where

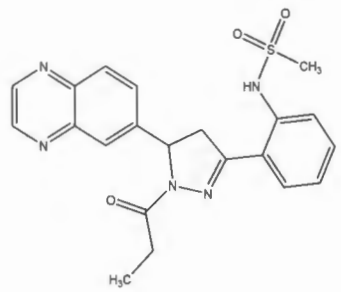
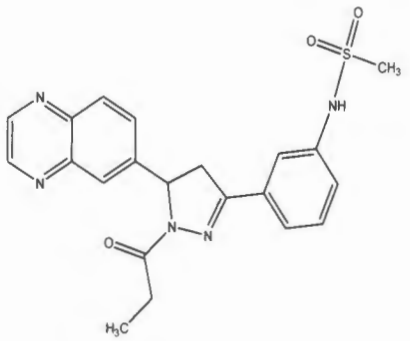
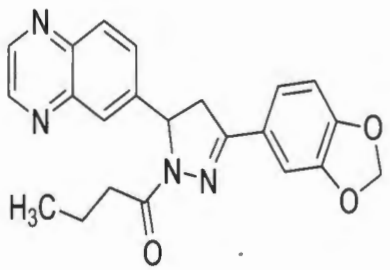
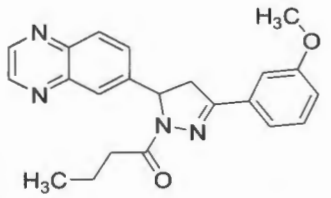
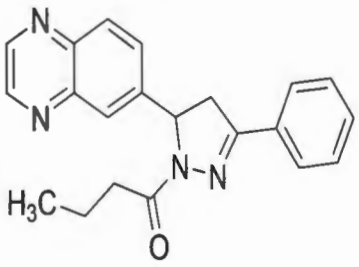
temperature changes are involved and in the preformulation phase of new compounds where only a small quantity of the compounds is present [13].

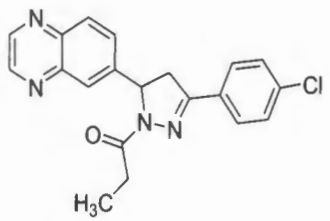
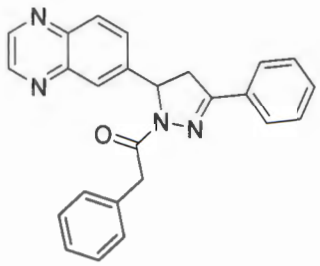
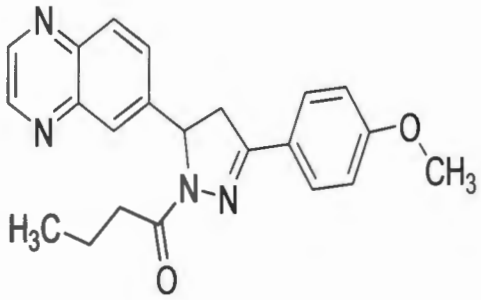
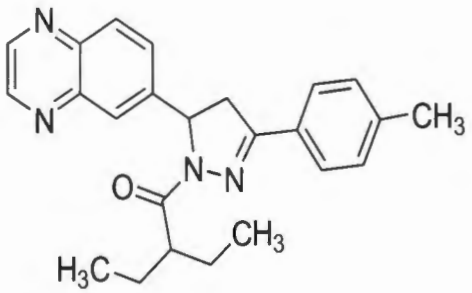
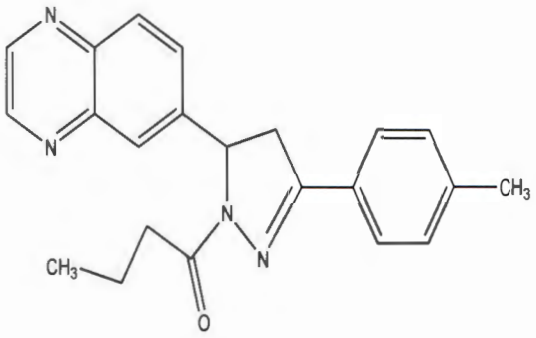
Thermophysical properties is required to develop new pharmacologically active compounds and their mechanism of action, in drug's metabolism processes including biological activities of the metabolites, stereochemistry importance in drug design, and to determine space which drug occupies [1]. To characterize the properties of the quinoxalines in pharmaceutical application solvents assists in finding out correlations amongst the structure and topology of the molecules with their partitioning, solubility and solvation properties [14].

In this study, twelve quinoxaline derivatives were examined. The name and structure of derivatives are given in **Table 1.1**

Table 1.1 Derivatives of quinoxaline used in the study

S.No	Structure	Name
1		(N-{-3-[1-methanesulfonyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl] phenyl} methane sulphonamide, MQDPMS
2		N-{2-[1-acetyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl]phenyl}methanesulfonamide, AQDPMS

3		N-{-2-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihdro-1H-pyrazol-3-yl] phenyl} methane sulphonamide, 2PQDPMS
4		N-{-3-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-3-yl] phenyl} methane sulphonamide, 3PQDPMS
5		1-[3-(2H-1,3-benzodioxol-5-yl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl]butan-1-one, BQDB
6		1-[3-(3-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl]butan-1-one, 3MQDP
7		1-[3-phenyl-5-quinoxalin-6-yl-4,5-dihydropyrazol-1-yl]butan-1-one, 3PQDB

8		1-(3-(4-chlorophenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl]propan-1-one, 4CQDPP
9		2-phenyl-1-[3-phenyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]ethan-1-one, 2PQDE
10		1-[3-(4-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl] butan-1-one, 4MQDPB
11		2-ethyl-1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one, 2EQDPB
12		1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one, 4MQDB

1.2 The importance and applications of quinoxaline derivatives

Among the various classes of nitrogen containing heterocyclic compounds, quinoxaline derivatives are the important components of several pharmacologically active compounds [15-20]. Although rarely described in nature, synthetic quinoxaline ring is part of number of antibiotics such as echinomycin and actinomycin which are known to inhibit the growth of gram-positive bacteria and are also active against various transplantable tumors [21].

In the pharmacological industry, they are considered promising molecules since they show biological properties [2, 22-25] such as antibacterial, antifungal, anticancer, etc., and neurological activities, among others. All these activities are possible due to the quinoxaline structure since its nucleus, can act as a precursor to assembly a large number of quinoxaline derivatives, which consequently, provide a large number of new compounds with biological applications.

Some new quinoxaline derivatives were synthesized recently and screened in vitro for their ability to inhibit the growth of *E.histolytica*. Many quinoxaline derivatives have wide application as dyes, electroluminescent materials, organic semiconductors, cavitands, chemically controllable switches and DNA cleaving agents [26-30]. They also serve as useful rigid subunits in macro cyclic receptors or molecular recognition [31].

Quinoxaline and its derivatives are important in modern drug research because of their extensive biological activities [19, 32-34] . Quinoxalines play an important role as basic skeleton for design of a number of antibiotic, anticancer and antiviral drugs. Many of the antimalarial [35], antifungal [36], antibacterial [37], anti-HIV, antidiabetic, antiviral [38] drugs contain quinoxaline nucleus. A slight change in the substituent(s) attached to the quinoxaline derivative remarkably affects the biological activity of the drugs.

1.2.1 Industrial Applications

Quinoxaline and its drivatives are also useful in industries as metal corrosion inhibitors, in Cu^{2+} detection in colorimetric sensors and phosphorescent organic light emiting diodes (PHOLEDs).

1.2.1.1 Corrosion inhibitior

Acids are widely used in industries, (especially hydrochloric acid) in acid pickling, acid cleaning, acid descaling and oil acidizing. It is also used to remove oxide layer from metallic parts before applying coating. The use of acid solution in industry leads to the corrosive attack on metal. Therefore, inhibitors are commonly used to minimize metal dissolution and acid consumption. Some organic compounds which mainly contain oxygen, sulphur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surface are used as efficient inhibitors in industries [39-46]. Many N-heterocyclic compounds have been proved to be effective inhibitors for the corrosion of metals and alloys in aqueous media [47-54].

2, 3-Quinoxalinedione (QD) (**Fig. 1.2**) was tested as corrosion inhibitor for mild steel in 1M HCl solution using electrochemical (potentiodynamic polarisation) and non-electrochemical (weight loss and UV–vis spectrophotometric measurement) technique. The results showed that this compound has good inhibiting properties with 88% efficiency approximately at a concentration of 10^{-3} M.

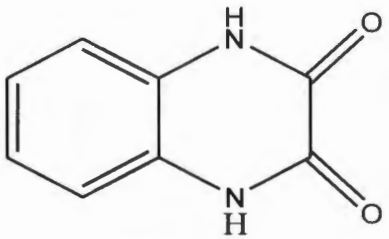


Fig 1.2 2, 3 -quinoxalinedione (QD).

Indeno-1-one [2, 3-*b*] quinoxaline (INQUI) (**Fig 1.3**) was synthesized and tested as corrosion inhibitor for mild steel in 0,5M H_2SO_4. The results showed about 81% of

inhibition efficiency at 10^{-6}M. This efficiency increases with INQUI concentration but decreases with immersion time [55].

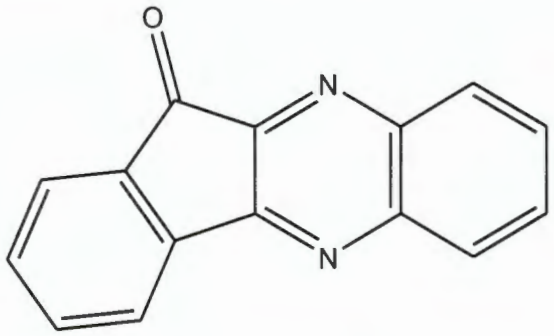


Fig 1.3 Indeno-1-one [2, 3-b] quinoxaline (INQUI).

1.2.1.2 Cu^{2+} detection

Transition metal ions are crucial in the life processes [56, 57]. Among these ions, Cu^{2+} plays an important role as a catalytic cofactor for a variety of metallo-enzymes such as superoxide dismutase, cytochrome oxidase, lysyl oxidase and tyrosinase etc. [58]. However when overloading, exhibit toxicity and could cause a variety of neurodegenerative diseases [59]. Though copper is an essential trace element, it is a major constituent in environmental pollution [60]. The formulation of copper-containing pesticides uses various forms of copper, which in the end dissociates into Cu^{2+}.

Nowadays, there are a number of technologies developed to detect Cu^{2+} such as inductively coupled plasma detectors, surface-plasmon resonance detectors, fluorescence anisotropy assays, quantum-dot-based assays, electrochemical sensors and fluorescence sensors. Although these technologies detect, Cu^{2+}selectively with high sensitivity need more sophisticated instruments and trained operators. On the other hand, it is possible to use naked-eye detection method, which gives a more fast response without involving any costly instrument, although it is a method with lower sensitivity and only give a qualitative response [56]. Therefore, the development of colorimetric receptor for heavy metal ions particularly for Cu^{2+} has become very important.

A simple ninhydrin–quinoxaline based colorimetric receptor was designed, synthesized and characterized. It exhibited high sensitivity and selectivity for Cu^{2+} in aqueous medium over a wide variation of cations such as Na^{+}, Mg^{2+}, Al^{3+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+}. When Cu^{2+} was added to the receptor solution it gave a clear colour change from olive green to pink. The detection limit of the receptor was found to be 3.43×10^{-7} M which is the lowest concentration for the Cu^{2+} in an aqueous solution by any naked-eye receptor [56].

1.2.1.3 Organic light emitting diode (OLED)

Phosphorescent organic light emitting diode (PHOLEDs) have gained much attention in research because of high efficiency. They are used to design and synthesis new compounds as hosts, charge transporting materials, and emitters [61]. PHOLEDs are able to harvest both singlet and triplet excitons for light emission [61-64].

Triplet emitters show long emissive lifetimes but less efficiency because of concentration quenching and triplet–triplet annihilation during device operation. One way to improve the performance of phosphorescent OLEDs is to use bipolar host materials. Bipolar host materials, contribute to the balanced transport of carriers and help to increase the probability of carrier recombination. In addition to the bipolar nature, the host materials should have amorphous nature for better device stability. Carbazole derivatives are widely used as host materials because of their high triplet energy and good hole-transporting properties.

New series of carbazole/quinoxaline hybrids with 1, 3, 5-benzene core have been synthesized. These compounds showed excellent thermal and morphological stabilities, because of their twisted geometry of the molecules. The bipolar nature along with high thermal stability and electrochemical properties allow these compounds to be used as host materials in red and green phosphorescent based OLEDs [63].

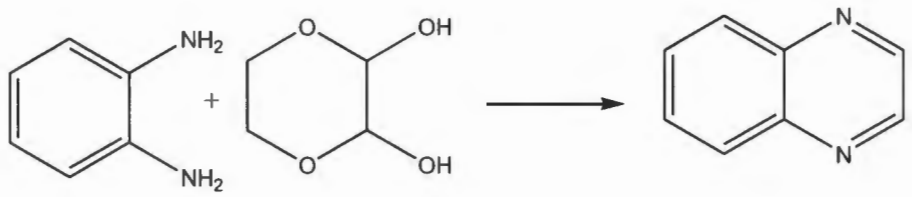
1.3. Properties and preparation of quinoxaline

Quinoxalines are soluble in water and produce monoquaternary salts when treated with quaternizing agents, like dimethyl sulphate and methyl p-toluene sulphonate. Chemically, quinoxaline is a low melting solid, m.p 29-30 °C purified by distillation, and a fraction of boiling point 108–111 °C [3, 4]. Quinoxaline has a dipole moment of 0.51 Debye, and their first and second ionization potentials, measured by photon electron spectroscopy, are 8.99 and 10.72 eV, respectively **(Table 1.2)** [3]. Most of the quinoxaline derivatives are synthetic and rare [65, 66] in natural state such as echinomycin and triostin-A.

Table 1.2 Properties of quinoxaline [3].

Properties of quinoxaline	
Formula	$C_8H_6N_2$
Molecular Weight	130.15
Melting temperature	29-30^{0}C
Natural State	White crystalline powder
Acidity	0.56 pKa
Dipole Moment	0.51 D
First ionization energy	8.99 Ev
Second ionization energy	10.72 Ev

The common procedure for synthesizing quinoxaline is condensing o-substituted benzene with a two carbon synthon. Therefore, quinoxaline is prepared from the reaction between o-phenylenediamine and 2, 3-dihydroxy-1,4-dioxane **(Fig 1.4).**



O-phenylenediamine 2,3-dihydroxy-1,4-dioxane Quinoxaline

Fig 1.4 Preparation of quinoxaline.

1.4. Activities of quinoxaline and its derivatives

1.4.1. Biological activity

The study of quinoxaline and its derivatives has become more important in recent years because of their wide variety in biological activity [6, 22-25, 27, 64] such as antibacterial, antifungal, anticancer, antitubercular, antileishmanial, antimalarial, antidepressant, antimycobacterial, anticandida, and neurological activities etc. Although rare in nature, synthesized quinoxaline and its derivatives are very much used in various antibiotics such as echinomycin, levomycin which are known to inhibit Gram-positive bacteria and also active against various transplantable tumors [4, 65]

1.4.2. Antimicrobial activity

Antimicrobial activities are the activities against bacteria, fungi, and mycobacterium species, called antibacterial, antifungal, antitubercular activity respectively. In the literature numerous quinoxaline derivatives show antimicrobial activity.

1.4.2.1. Antibacterial activity

Diarrhea and invasive dysentery cause by *Escherichia Coli* are the fatal infectious diseases. Abscess of the brain is a complication of Escherichia coli infection. Salman Ahmad Khan et. al 2007 [68] synthesized 3β-Chloro-5α-cholastan-6-[thiazolo (4,5-b)quinoxaline-2-yl-hydrazone] and screened for in vitro antibacterial activities against Escherichia Coli. Gauri Gupta and Preeti Verma 2014 reported 2,3-diphenylquinoxaline **(Fig 1.5),** 2-(2-methylphenyl)-

3-phenylquinoxaline-6-sulfonamide **(Fig 1.6)** were synthesized and evaluated with anti-bacterial activity.

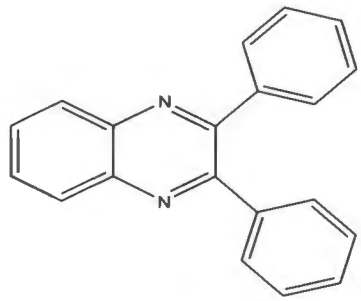


Fig 1.5 2,3-diphenylquinoxaline.

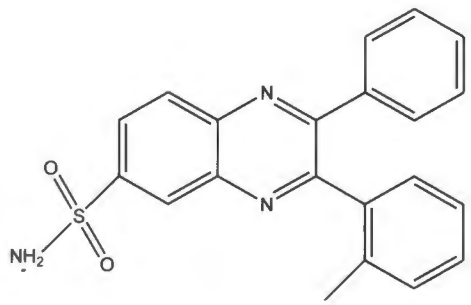


Fig 1.6 2-(2-methylphenyl)-3-phenylquinoxaline-6-sulfonamide

1.4.2.2. Antitubercular activity

Tuberculosis (TB) is a contagious disease which is infected by Mycobacterium tuberculosis. About 3 million people die every year from TB and are infected especially in developing countries [66-69]. Several studies on the compounds 7-chloro-3-(p-substituted)-phenylaminoquinoxaline -2-carbonitrile-1,4-di-N-oxide, 6,7-dichloro-2-ethoxycarbonyl-3-methylquinoxaline-1,4-di-N-oxide and 3-acetamide-6,7-dichloroquinoxaline-2-carbonitrile-1,4-di-N-oxide have been shown to possess M. tuberculosis growth inhibition values 99 to 100% [70].

The compound 3-methyl-2-phenylthioquinoxaline 1,4-dioxides showed good activity against Mycobacterium tuberculosis in a preliminary in vitro evaluation and exhibited minimum inhibitory concentration (MIC) between 0.39 and 0.78 μg mL^{-1} (rifampicin MIC = 0.25 μg mL^{-1}) [22]

1.4.2.3. Antiviral activity

Viruses are small infectious agents that can infect all types of organisms, from animals and plants to bacteria [71]. Viruses such as Herpes simplex virus type 1 (HSV-1) and type 2 (HSV-2) belonging to the Herpesviridae family [72] can cause various illnesses from asymptomatic infection to fulminant disseminated diseases, including labials herpes, keratitis, genital herpes, and encephalitis [73, 74].

Researchers continue to search new variety of antiviral drugs for HSV infection. Different types of quinoxaline derivatives show antiviral activity. Novel series of al 6H-indolo-[2, 3-b] quinoxalines were synthesized and evaluated for their antiherpes virus activity and the compound 2, 3-dimethyl (dimethylaminoethyl)-5H-indolo-[2,3-b]quinoxaline had the major antiviral activity. It was proved that the compound 2, 3-dimethyl-6-(dimethylaminoethyl)-6H-indolo-(2, 3-b) quinoxaline showed high activity against HSV **(Fig.1.7)** [2]. Human immunodeficiency virus type 1 (HIV-1) causes acquired immunodeficiency syndrome (AIDS) [75, 76].

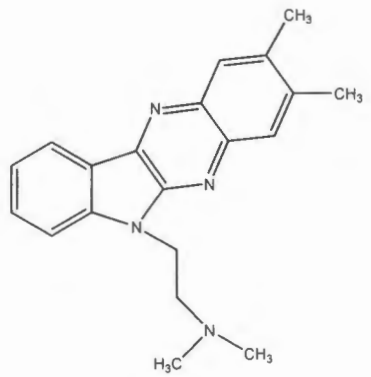


Fig 1.7 2, 3-dimethyl-6-(dimethylaminoethyl)-6H-indolo-(2,3-b)quinoxaline.

6-chloro-3, 3-dimethyl-4-isopropenyloxycarbonyl-3,4-dihydroquinoxaline-2-[1H]- thione **(Fig. 1.8)** was synthesized and evaluated for enzyme activity. It was found to be very potent inhibitor for both HIV-1 RT activity and HIV-1 replication in tissue cultures although, ineffective against human immunodeficiency virus type 2 (HIV-2-RT) [73]

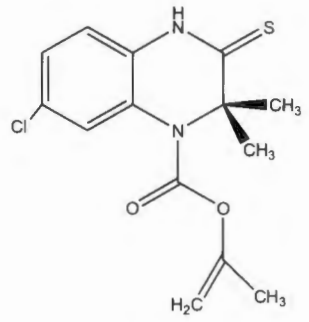


Fig 1.8 6-chloro-3, 3-dimethyl-4-(isopropenyloxycarbonyl)-3, 4- dihydroquinoxaline-2-[1H]-thione.

A library based on 2, 3-difuryl-4-quinoxaline-R-metilcarboxamide derivatives **(Fig 1.9)** with 2-furyl groups at position 2 and 3 and phenyl group in position 6 through an amide linker has been prepared in literature. Among all the compounds in the library, the compound listed in fig.1.9 has shown the highest effectiveness being the R the possible substituents. Also the compound 2 was able to inhibit influenza a virus growth [71].

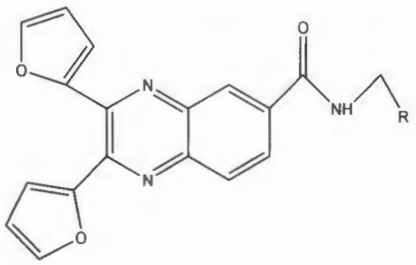


Fig 1.9 2, 3-difuryl-4-quinoxaline-R-metilcarboxamide derivatives
(Compound 1 R = 3-O-Me-ph- ; Compound 2 R = 2-Furyl-)

1.4.3. Antifungal activity

One of the most common fungal infection is candidiasis, caused by Candida albicans a fungus that grows both as yeast and filamentous cells. This fungus can be resistance to antimycotic drugs which are available in the market [77]. Therefore it was necessary to search for new effective drugs and treatments. Thieno [2, 3-d] pyrimidines and pyrrolo [3,4-b] quinoxalines were synthesized and were tested for their antifungal activity against Candida albicans [67]. Substituted 3-benzylquinoxalines were synthesized from o-phenylenediamine and phenyl pyruvic acid. The compounds showed good antifungal activity.

1.4.4. Antiprotozoan activity

1.4.4.1 Antiamoebic activity

Entamoeba histolytica is a protozoan responsible for the amoebiasis infection [78, 79] . It causes amoebic colitis, brain and liver abscess. Amoebiasis is the second leading cause of death word-wide [80]. More than 50 million people are infected [81]. Though there are numerous antiamoebic compounds such as nitroimidazoles used in market, they are not effective, raising the possibility of drug resistance, leading to the search of new compounds [82].

1-[thiazolo[4-5b]quinoxaline-2-yl]-3-phenyl-2-pyrazolines derivatives **(Fig 1.10)** synthesized were found to be a potent inhibitor of HM1:IMSS strain of E. histolytica, where the presence of 3-Bromo or 3-chloro substituents on the phenyl ring and 4-methyl group on the pyrazoline ring showed a greater extent of antiamoebic activity [82].

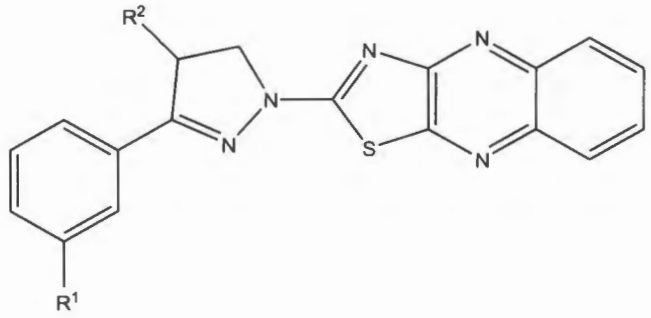


Fig 1.10 1-[thiazolo [4-5b] quinoxaline-2-yl]-3-phenyl-2-pyrazolines core.

In this study, metronidazole was used as the reference drug and had 50% inhibitory concentration (IC_{50}) in the range of 1.69 to 1.82 μM. The compound (6) was the most active and showed the great effectiveness (**Table 1.3**).

Table 1.3 In vitro antiamoebic activity of 1-[thiazolo[4-5b]quinoxaline-2-yl]-3-phenyl-2-pyrazolines derivatives against HM1:IMSS strain of Entamoeba histolytica ([a]Standard Deviation) [82].

Compound	R^1	R^2	IC_{50}μM	SD[a]
1	H	H	6.76	0.20
2	Br	H	4.98	0.11
3	Cl	H	1.09	0.08
4	H	CH_3	2.34	0.23
5	Br	CH_3	1.45	0.14
6	Cl	CH_3	0.72	0.10
Metronidazole	-	-	1.69	0.24

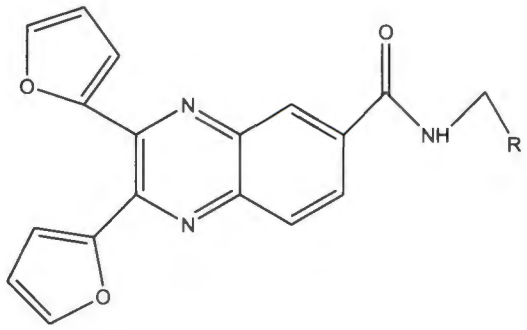


Fig1.11 2,3-Difuryl-4-quinoline(R)metilcarboxamide deravatives.

1.4.4.2. Antiparasitic activity

Leishmaniasis and Malaria are parasitic diseases which occur in tropical and sub-tropical areas of the world. Leishmaniasis is caused by protozoan of the genus Leishmania and Malaria by Plasmodium falciparum leading to over a million deaths annually [71, 83].

Most of the drugs available for these diseases are expensive and needs long time treatment and also are becoming ineffective [24, 84]. Therefore, it requires the development of cheaper and more effective drugs. Recently, Barea et.al [24] synthesized 14 new 3-amino-1,4-di-N-oxide quinoxaline-2-carbonitrile derivatives which were evaluated for their in vitro antimalarial and antileishmanial activity against plasmodium falciparum Colombian FCR-3 Strain and Leishmania amazonensis Stain MHOM/BR/76/LTB-012A.The study showed that the compounds with one halogenous group substituted in position 6 and 7 of the quinoxaline ring were most active and provided an efficient approach for further development of antimalarial and antileishmanial agents.

1.4.5. Chronic and metabolic disease bioactivity

1.4.5.1. Antidiabetic activity

Diabetes mellitus, commonly referred to as diabetes, is a metabolic disease in which there is high blood sugar levels over a prolonged period. Symptoms of high blood sugar include frequent urination, increased thirst, and increased hunger.

Diabetes type 1 is insulin-dependent and type 2 is non-insulin-dependent. Diabetes type 1 patients require subcutaneous injection insulin daily, while diabetes type 2 patients can be treated with several drugs such as sulfonylureas, nateglinide, and biguanides etc. [25, 85] . Since these drugs cause side effects [85], it was necessary to discover some new compounds. Therefore, some transition metal complexes of quinoxaline-thiosemicarbazone ligands L^1H_2 and L^2H_2 (**Fig.1.12**) have been synthesized and the ligands were explored with copper and zinc complexes in diabetes induced Wister rats. It was observed that the compounds [Zn L^1 (H_2O)] and L^2H_2 showed prominent reduction in blood glucose level and the complexes [$CuL^1(H_2O)$], $ZnL^1(H_2O)$] and [$CuL^2(H_20)$ exhibit good activity in oral glucose tolerance test (OGTT) with low toxicity [25].

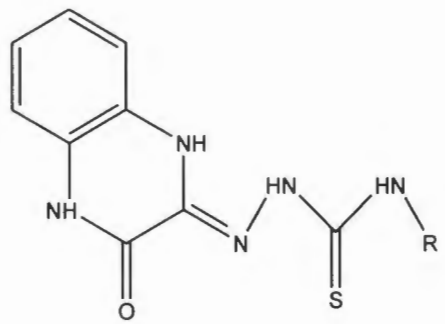


Fig 1.12 Ligands L^1H_2 and L^2H_2 for L^1H_2, R = CH_3 and for L^2H_2, R = C_6H_5

And also the compounds (N-arylcarbamoyl and N-aryl thiocarbamoyl) hydrazine-quinoxaline-2-(1H) (**Fig.1.13**) have been reported as mild hypoglycaemic agents [2].

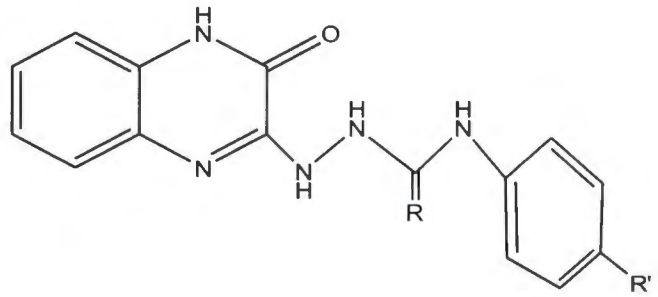


Fig 1.13 (N-arylcarbamoyl and N-aryl thiocarbamoyl) hydrazine-quinoxaline-2-(1H).

R = O, S and R' = H, F

1.4.5.2. Anti-inflammatory activity

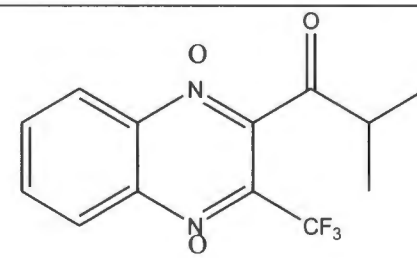
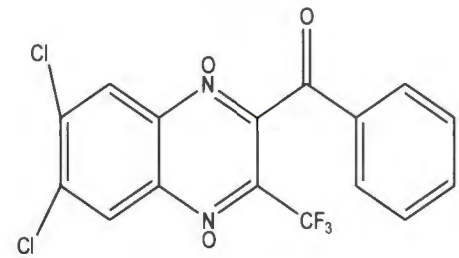
Generally, for the treatment of pain and inflammation, non-steroidal anti-inflammatory drugs (NSAIDs) are widely used in therapeutics. Long-term usage of these drugs lead to significant side effects. Therefore, it was necessary to discover new ant-inflammatory drugs [86, 87]. Quinoxaline 1,4-di-N-oxide derivatives such as 4-(7-fluro-3-methyl-quinoxaline-2-yl)-6-(3,4,5-trimethoxy-phenyl)-pyrimidin-2-ylamine and 2,6,7-trimethyl-3-[5-3,4,5-trimethoxy-phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-quinoxaline showed an in vivo anti-inflammatory. activity, higher than one reference drug, IMA (indomethacin),and in vitro decreasing value of LOX (lipoxygenase). Lipoxygenase is an enzyme essential to arachidonic acid (AA) metabolism which leads to the formation of leukotrienes, a type of proinflammatory mediator involved in process like fever, asthma and cardiovascular disease [88, 89]. It was been proved that the incorporation of pyrimidine, thiazolopyrimidine, pyrazolopyridine, pyridopyridine, p-chlorophenyl, p-methoxyphenyl or pyridine nucleus to quinoxaline moiety cause significant anti-inflammatory activity and also analgesic.

Also 4-alkoxy-6, 9-dichloro [1,2,4] triazalo[4,3-a] quinoxalines were synthesized and ant-inflammatory effect was tested as inhibitors of the pro-inflammatory cytokines TNF-α and IL-6 [90]. The results revealed efficiency in both cytokines.

1.4.5.3. Anticancer activity

Since quinoxaline nucleuses exhibit potential anticancer activity, and can be used to prepare various anticancer drugs [72]. A new series of 2-alkylcarbonyl and 2-benzoyl-3-trifluromethylquinoxaline-1,4-di-N-oxide derivatives was synthesized and evaluated for in vitro antitumor activity against a 3-cell line panel McF_7 (breast), NCIH 460 (lung) and SF-268 (CNS), and then evaluated in full panel of 60 human tumor cell lines, derived from nine cancer cell types. It was studied that anticancer activity depends on the substituents in the carbonyl group and follows the increasing activity in the order: ethyl < isopropyl < tert.butyl < phenyl-ones. Among these, the following compounds 1 to 5 **(Table 1.4)** showed higher anticancer activity and were the most active with the following mean G_{I50} (Growth Inhibition) values **(Table 1.5).**

Table 1.4 Chemical structure of compounds 1 to 5.

Compound	Name	Chemical structure
1	2-Isobutyl-3-trifluromethyl quinoxaline1,4-di-N-oxide.	
2	2-benzoyl-6,7-dichloro-3-trifluromethylquinoxaline 1,4-di-N-oxide	

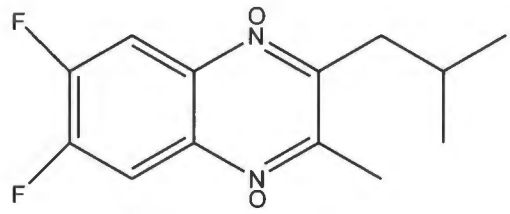
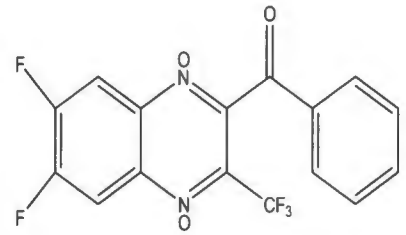
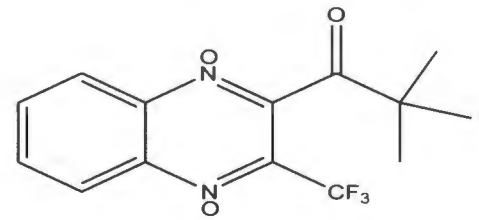
3	6,7-difluro-isobutyryl-3-trifluromethylquinoxaline1,4-di-N-oxide	
4	2-benzoyl-6,7-difluro-3-trifluromethylquinoxaline1,4-di-N-oxide	
5	2-(2,2 dimethylpropanoyl) - 3-trifluromethylquinoxaline1, 4-di-N-oxide.	

Table 1.5 In vitro inhibitory activity test for compounds 1 to 5 against 60 human tumor cells lines [23].

Compound	IG_{50} μM
1	1.02
2	0.42
3	0.52
4	0.15
5	0.49

1.4.5.4. Antiglaucoma activity

Glaucoma is a type of optic neuropathy associated with characteristic optic nerve damage which may lead to certain visual field loss patterns at least some part of which is due to a sub optimal intra ocular pressure [91]. Almost 67 million people world-wide are affected by Glaucoma. Glaucoma remains the leading cause of irreversible blindness responsible for 14% of blindness after Cataract and Trachoma [92]. Alphagan **(Fig.1.14)** is a relatively selective alpha-2-adrenergic receptor agonist which is a quinoxaline derivative consists of (5-bromo-N-(4,5-dihydro-1H-imidazol-2-yl)-6-quinoxaline. Since this drug has power to reduce the intraocular pressure, it serves as anti-glaucoma agent.

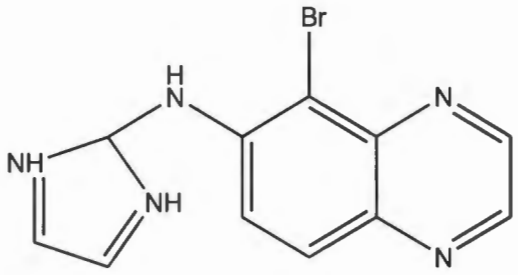


Fig 1.14 Alphagan.

1.4.5.5. Antiproliferative activity

Atherosclerosis causes heart attack, stroke and gangrene of the extremities for 50% of all mortality in USA, Europe and Japan [93]. After artery injury, abnormal proliferation and migration of vascular smooth cells (SMCs) into the intimal layer of the arterial wall occurs, proliferating and synthesizing extracellular matrix components, playing an important role in coronary artery atherosclerosis and restenosis after an angioplasty [67, 94].

A series of 6-arylamino-2, 3-bis (pyridine-2-yl)-7-chloroquinoxaline-5, 8-diones **[Fig 1.15]** were synthesized and tested for their inhibitory activity on rat aortic smooth muscle cell (RAoSMC) proliferation.

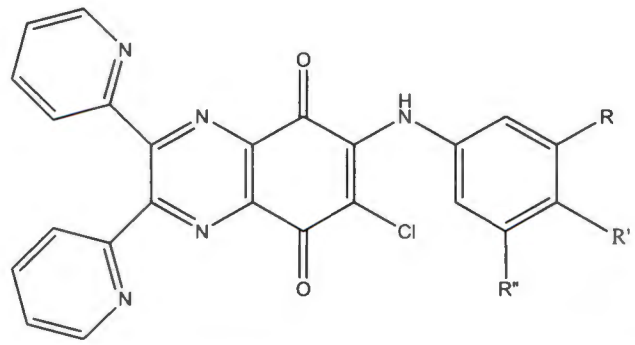


Fig 1.15 6-arylamino-2, 3-bis (pyridine-2-yl)-7-chloroquinoxaline-5,8-diones

Possible substituents R, R' and R'' of the compound are represented in Table (6). Inhibition Concentration values (IC_{50}) were determined and compared with positive control mycophenolic acid (MPA) **(Table 1.6).** It was observed that most of the compounds showed good activity and the quinoxaline-5, 8-diones were found to be potent antiproliferative agent [72, 95].

Table 1.6 Structures and IC_{50} values of 6-arylamino-2,3-bis(pyridine-2-yl)-7-chloroquinoxaline-5,8-diones for inhibition of SMC proliferation [95].

Compound	R^1	R^2	R^3	SMC IC_{50} (μL)
2a	H	Cl	H	1.5
2b	H	OH	H	5.5
2c	H	F	H	1.0
2d	H	CF_3	H	1.1
2e	H	OCF_3	H	1.0
2f	H	OCH_3	H	3.5
2g	H	H	H	3.1
2h	Cl	Cl	H	1.0
2i	F	F	F	1.2

1.4.5.6. Antidepressant activity

5-Hydroxytryptamine (5HT) is a neurotransmitter, commonly known as serotonin. It is used in a number of physiological and patho-physiological processes, acting through the receptor subtypes, from 5-HT_1 to 5-HT_7. Most of the receptors subtypes belong to the family of G-Protein coupled receptor (GPCR) but the receptor subtype $5HT_3$ is a ligand gated ion channel [67, 96].

The antagonists receptor lead to various responses such as anti-emetic action in cancer chemo-/radio-therapy induced nausea and vomiting, ant-depressant, anxiolytic, anti-psychotic and anti-inflammatory. Since the drugs available for depression conditions have a delayed onset of action. Therefore there is need to discover new antidepressant drugs for safer and faster action [67, 96].

1.4.5.7. Antiglutameric activity

Glutamic acid which is a major excitatory neurotransmitter in the central nervous system in mammalian species is an excitatory amino acid (EAA). Overstimulation of the postsynaptic glutamate receptors occurs, due to a high release of excitatory amino acid lead to neuronal death, and consequently induce neurodegenerative disorders such as Alzheimer and Huntington's disease [97-101].

AMPA-R (α-amino-3-hydroxy-5-methyl-4-isoxazole-propionic acid receptor) antagonists have showed no side effects such as schizophrenia and protective activity in neural death. A number of quinoxalinedione derivatives which have AMPA-R antagonistic activity have been synthesized and tested against the EAA receptor [102] . The compound 7-[[4-[*N*-[4-carboxyphenyl]carbamoyloxy]methyl]imidazolyl]-3,4-dihydro-6-nitro-3-oxo-quinoxaline-2-carboxylic acid (GRA-293) was synthesized and identified as a novel AMPA-R antagonist due to its high potency and good selectivity *in vitro*, and its potent neuroprotective effects in an animal model *in vivo*, higher than the known quinoxalinedione compounds used.

These effects are due to a novel substituent, namely substituted benzene ring with urethane linkage to imidazole, in C-7 position, which leads to a potent AMPA-R affinity and contributes to therapeutic efficacy in animal models. This compound, with such characteristics, is used in the treatment of acute cerebral ischemia [102].

1.5 Thermophysical and thermodynamic properties, together with their importance

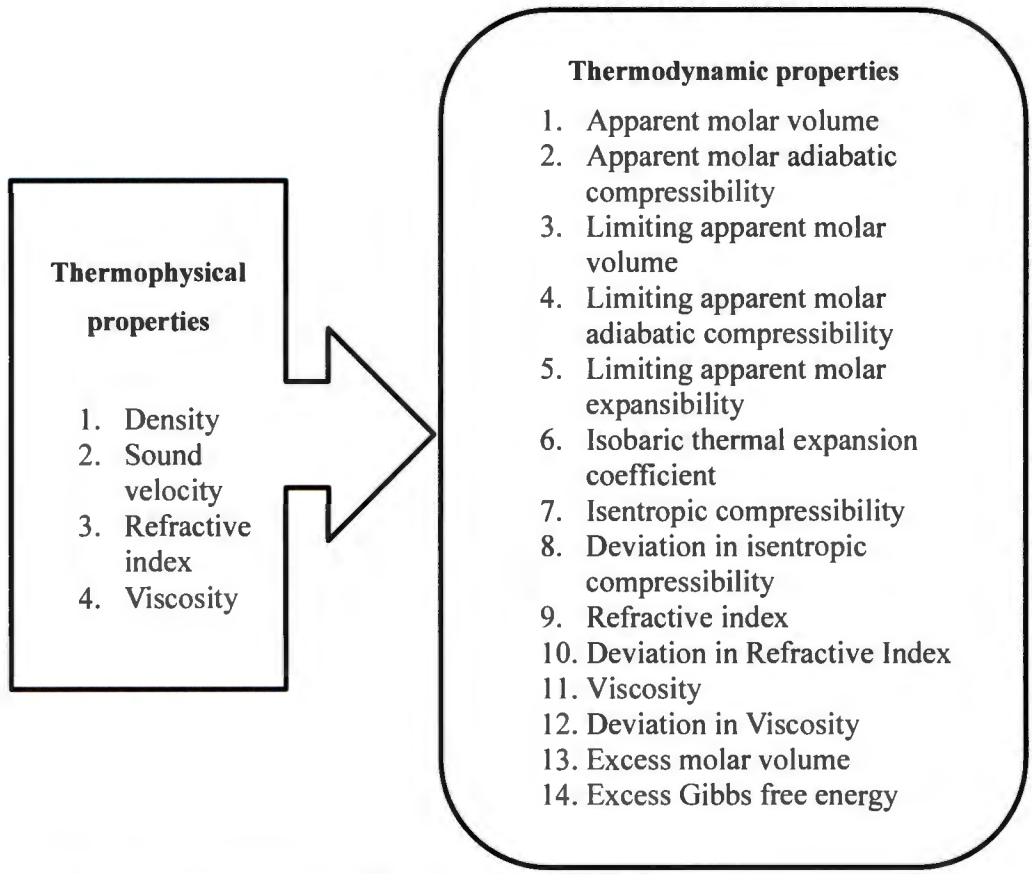


Fig 1.16 Classification of Thermophysical and Thermodynaic properties.

Thermodynamic and thermophysical property data are essential in different industries such as oil and gas for flow assurance and oil recovery, in the chemical for the design of separation processes, in the pharmaceutical and polymer for solvent selection and emission. These data are also necessary in the environmental science for the estimation of the distribution of

chemicals in various ecosystems, in biotechnology for the origin of many diseases traced to aggregation of proteins and several protein separations [103].

Furthermore, these data provide information about the interactions such as solute-solute, solute-solvent and solvent-solvent [104-106] and allows for developing new reliable correlations and/or predictive models and to test the solution theories for quinoxaline compounds and their mixtures with methyl acetate.

Therefore, there is a need for thermophysical and thermodynamic properties such as: density, sound velocity, viscosity, refractive index, excess molar volume, excess isentropic compressibility, deviation in refractive index, deviation in viscosity, excess Gibbs free energy, apparent molar volume and apparent molar adiabatic compressibility [107].

These properties of quinoxaline deravatives solutions have proved particularly informative in elucidating the solute-solute, solute-solvent and solvent-solvent interactions that exist in these solutions. The information about thermophysical properties with their dependency on temperature and concentration is also important for use in chemical engineering design in applications that include surface facilities, pipeline systems and mass transfer operations. To the best of our knowledge, there are few studies has carried out on thermophysical properties of quinoxaline derivatives, but there are no data reported for the binary systems such as Methyl acetate + aqueous or alcohol solution of quinoxaline derivatives.

In view of the above, the thermophysical properties of quinoxaline compound and their binary mixtures with organic solvents at several temperatures and concentration is being carried out in this thesis.

1.6 Aims and objectives of the research

The main purpose of this research is to carry out an extensive investigation of thermophysical and thermodynamics properties of twelve (12) selected derivatives of quinoxaline with methyl acetate at various cocentrations and temperatures.

The objectives are as follows to:

- measure the thermophysical properties such as density and sound velocity for the binary systems of aquoues/alcoholic solution of quinoxaline deravatives with methyl acetate at various temperatures and concentration.
- investigate the effect of temperature and concentration on these properties and their derived properties.
- investigate the effect of different derivatives on intermolecular interactions such as solute-solute, solute-solvent, solvent-solvent which takes place in solution.
- study the interactions between the quinoxaline compounds and other solvents at different concentration and temperature.

CHAPTER 2

LITERATURE REVIEW

Literature search has been done on the studies such as density and sound velocity measurements of quinoxaline derivatives with solvents at different temperature but no articles have been found in open literature related to the present studies. The articles available are in different types of studies such as synthesis of quinoxaline derivatives, used and application of quinoxaline derivatives etc. which is reported in literature review. Therefore, the studies performed in this work is completely new and have a good impact on area of thermodynamics of solution research using quinoxaline derivatives.

Patidar *et al.* [4] presented a review article on the history, chemistry, synthesis and applications of quinoxaline derivatives. Quinoxaline is also called as benzopyrazine. It is a heterocyclic compound fused with benzene and pyrazine ring. Quinoxaline is a white crystalline with a low melting solid with melting point 29-30^{0}C and is miscible with water. Since it is weakly basic with pKa 0.56 it forms salts with acids. When quinoxaline is treated with conc. HNO_3, oleum, it forms 5-nitroquinoxaline and 5, 7-dinitroquinoxaline. With alkaline potassium permanganate, quinoxaline is oxidised to form pyrazine 2, 3-dicarboxylic acid. Quinoxalines are synthesized in a few minutes by the condensation reaction of O-phenylenediamine with α-dicarbonyl compounds in ethanol under microwave irradiation. The advantages of this methods are pure and high yield product, short reaction time, using ethanol instead of expensive solvent for isolation of products.

Pereira *et al.* [108] in their state of art review reported a summary of the progress made over the past years, in the knowledge of structure and mechanism of the quinoxaline and its derivatives which were associated with medical and biomedical value, as well as industrial value. In addition, they also added that by modifying quinoxaline structure it is possible to obtain a wide variety of biomedical applications, namely antimicrobial, ant diabetic,

antiproliferative, anti-inflammatory, anticancer, antiglaucoma, antidepressant activities, chronic and metabolic diseases treatment.

Maria *et al.* [109] reported on the derivatives the mean (N-O) bond dissociation enthalpies for three 2-methyl-3-(R)-quinoxaline-1,4-dioxide(1) derivatives, with R = methyl (1a), ethoxycarbonyl (1b) and benzyl (1c). The standard molar enthalpies of formation in the gaseous state at T = 298.15 K for the three (1) derivatives were determined from the enthalpies of the combustion of the crystalline solids and their enthalpies of sublimation. They used accurate density functional theory-based calculation to estimate the gas–phase enthalpies of formation for the corresponding quinoxaline derivatives. The first and second N-O dissociation enthalpies were also calculated and find the values to be in an excellent agreement with the experimental results.

2.1 Synthesis of quinoxaline deravatives

Fong Dong *et al.* [110] reported that task specific ionic liquid N, N, N –trimethyl-N-propanesulfic acid ammonium hydrogen sulphate [TMPSA]. HSO_4 was used as catalyst for the synthesis of quinoxaline derivatives. The products were separated from the catalyst by filtration and the catalyst was recycled and reused for several times without decreasing catalytic activity.

Heravi *et al.* [111] evaluated the speed of the reaction of the sysnthesis of quinoxaline deravatives from condensation of o-phenylenediamines and 1,2- dicarbonyl compounds at room temperature. Zn[(L)proline] was found to be an effective catalyst which gave an excellent yield, furthermore the catalyst was also found to be recyclable and reusable.

Khaksar *et al.* [112] reported a new, convenient, mild and efficient procedure for the synthesis of quinoxaline derivatives by the reaction of 1,2-diamines with 1,2-dicarbonyl compounds under mild reaction conditions in hexafluroisopropanol (HFIP). The solvent (HFIP) was readily separated from reaction products and recovered in excellent purity for direct reuse.

Heravi *et al.* [113] developed a convenient, eco-efficient and eco-friendly procedure for the synthesis of quinoxaline deravatives from the various 1,2- diketones and 1,2-diamines using catalytic amount of $CuSO_4$. $5H_2O$ under mild reaction conditions at room temperature. The reaction was performed in water as well as in ethanol. They also reported that their method represents the first example of synthesis of quinoxalines in water.

Sajjadifar *et al.* [114] evaluated the use of 3-methyl-1-sulfonic acid imidazolium hexafluorophosphate (v) [Msim][PF_6] and 3-methyl-1-sulfonic acid imidazolium tetrafluoroborate [Msim][BF_4] as a efficient recyclable ionic liquids catalysts for the synthesis of quinoxaline derivatives by the one-pot condensation reaction.

Bhattacharjee *et al.* [115] reported the synthesis of a number of quinoxaline derivatives by the reaction of 2-chloroquinoxaline with various substituted amines in the presence of pyridine. The reactions were carried out using conventional procedure and also under microwave irradiation. In microwave irradiation, it took a short time for completion of the reaction and the percentage yield was high whereas under conventional method it took a longer time and the percentage yield was low. They synthesized 1-(Quinoxalin-2-yl) thiosemicarbazide using conventional method and microwave irradiation method. The microwave irradiation method led to the formation of product in 10 min as compared to conventional method (5 days).The

percentage yield using microwave irradiation method was 90% as for conventional method was 30%.

Lainne *et al.* [116] reported on the synthesis of a series of quinoxaline derivatives and their activity against M. tuberculosis (Mtb) and mycobacterium avium (MAC) 4-acetoxybenzyl-2-quinoxalinecarboxylate and it was found to have excellent activity against Mtb but only modest activity against MAC.

Ajaikumar *et al.* [117] studied the synthesis of highly significant medicinally quinoxaline derivatives using liquid phase condensation reaction method from various 1,2-diamines with 1,2-diketones via binary metal oxides supported on Si-MCM-41 mesoporous molecular Sieves. A mixture of 1,2-diketones (5 mmol) , 1,2-diamine (5 mmol) and a freshly activated catalyst (0.2 g) in acetonitrile solvent (10 mL) was stirred at room temperature for the specified reaction time using a 25 mL round-bottomed flask. The progress of the reaction was monitored by TLC using hexane: dichloromethane (95:5) as an eluent. After completion of the reaction the catalyst was removed by filtration and the crude product was isolated by distillation under reduced pressure. The crude products were subjected to column chromatography using silica gel eluent (95:5 hexane: ethyl acetate), which gave quinoxaline in excellent yield. The products were analysed using ^{1}HNMR, ^{13}C NMR and FT-IR techniques

Yan *et al.* [118] reported a novel and efficient method for the synthesis of quinoxaline derivatives. Isopropylidenation of 4-chloro-4-deoxy-α-D-galactose with 2,2-dimethoxypropane, followed by selective hydrolysis, gave 2,3-O- isopropylidine-4-chloro-4-deoxy-D-galactose dimethyl acetal as a sole product. Oxidation of compound with $(Bu_3Sn)_2$ O-Br_2 gave corresponding hex-5-ulose derivative in high yields. The hex-5-ulose

derivative could react with o-phenylenediamines under neutral conditions produced quinoxaline derivatives in reasonable yields.

Budakoti *et al.* [119] reported the synthesis of chalcones, amino-5-substituted-(3-phenyl (2-pyrazolinyl) methane-1-thione derivatives and 2-(5-subtituted-3-phenyl-2-pyrazolinyl)-1,3-thiazoline [5,4-b] quinoxaline derivatives and investigated their in vitro antiamoebic activity against HMI: IMSS strain of E.histolytica. All the compounds were characterized by electronic, IR, ^{1}H NMR and mass spectroscopic data. It was observed that the antiamoebic activity was enhanced by modifying the structure of chalcones to the pyrazolines and further to quinoxalines.

Ghobadi *et. al* [120] developed a simple and practical method for the synthesis of quinolone deravatives by the reaction of 1,2-phenylenediamines with 1,2-diketones in the presence of sodium dodecyl sulfate (SDS). The reaction media which was used was aqueous at room temperature. All of the quinoxaline deravatives obtained (products) had a yield of more than 90%, which suggested than this method is not only simple and practical it is also convenient.

2.2 Quinoxaline deravatives as a corrosion inhibitors

Obot *et al.* [9] reported on the *s*ynthesis of 2,3- diphenylbenzoquinoxaline (2,3 DPQ) and its inhibiting action on corrosion of mild steel in 0.5 M H_2SO_4 by weight loss method at 30^0C and quantum chemical calculations to explain the mechanism of inhibitory action. The results of the investigation show that this compound exhibited excellent inhibitory properties for mild steel corrosion in H_2SO_4. They concluded that as the concentration of inhibitor increased inhibition efficiency increased. Using Langmuir adsorption model, the adsorption energy of 2, 3 DPQ on the mild steel surface was -114 KJmol^{-1}.

Obot *et al.* [55] reported the inhibitor Indeno-1-one [2,3-b] quinoxaline (INQUI) at inhibitor concentration of 2-10 x 10^{-6} M for the corrosion of mild steel in 0.5M H_2SO_4 using gravimetric method at 30^0C. The investigation results showed that the inhibitor INQUI has 81% efficiency at a concentration of 10 x 10^{-6}M. The inhibition efficiency increases as inhibitor concentration increased and decreased in immersion time. Density functional theory (DFT) proved that INQUI molecule is adsorbed on the mild steel surface by the most negatively charged N and O atoms.

Kumar *et al.* [61] reported a new synthesis and design of a calorimetric receptor based on a ninhydrin-quinoxaline derivative exhibiting high sensitivity and selectivity towards Cu^{2+} in aqueous medium over various cations such as Na^+, Mg^{2+}, Al^{3+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}. When they added Cu^{2+} to the receptor 1 solution, gave colour change from olive green to pink. The detection limit of Cu^{2+} by receptor 1 was calculated as 3.43 x 10^{-7}M which was the lowest in aqueous medium by any naked-eye receptor. Receptor 1 was better over all other colorimetric receptor for Cu^{2+} in terms of its detection limit, selectivity, response time, interference free detection and minimum use of organic solvent as a co-solvent with water. Therefore, these results were very useful for the construction of new colorimetric ICT (intramolecular charge transfer) probe based on ninhydrin-quinoxaline derivative.

Fu *et al.* [121] reported that quinoxaline and its derivatives act as an excellent inhibitors for the corrosion of mild steel in 1.0 M HCl at 25^0C using weight loss measurement and Tafel polarization technique. These measurements revealed that the inhibition efficiency increased with increase in the concentration of inhibitors, and the inhibition efficiency decreased in the order 4-(quinoxaline-2-yl) phenol (PHQX) > 2-quinoxalinethiol (THQX) > 2- chloroquinoxaline (CHQX) > quinoxaline (QX).

Abboud *et al.* [122] synthesised 2,3-Quinoxalinedione (QD) from the condensation reaction of 2 mol of 1,2-Phenylenediamine and 1 mol of oxalic acid in acidic media. Its inhibiting action on the corrosion of mild steel in 1M HCl solution was tested using electrochemical (Potentiodynamic polarization) and non-electrochemical technique (weight loss and UV-vis spectrophotometric measurement). The results of the investigation showed that this compound had good inhibiting properties for steel corrosion in HCl with efficiency of 88% at a concentration of 10^{-3} M. The adsorption behaviour of the investigated compound was determined by the Langmuir isotherm.

Obot *et al.* [123] reported on the synthesis of Acenaphtho [1,2-b] quinoxaline (AQ) and its effectivenes as a corrosion inhibitor for mild steel in 0.5M H_2SO_4. Using weight loss method. The results obtained showed that the compound AQ has 80% inhibition efficiency at 10 $x10^{-6}$ M. The inhibition efficiency increased by increasing concentration of AQ. The mechanism of inhibition action of AQ was studied by DFT.

Olasunkanmi *et al.* [124] investigated the effectiveness of various quinoxaline deravatives (1-[3-(4-methylphenyl)-5- (quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Me-4-PQPB), 1-(3-(4-methoxyphenyl)-5-(qui- noxalin-6-yl)-4,5-dihydropyrazol-1-yl)butan-1-one (Mt-4-PQPB), 1-[3-(3-methoxyphenyl)-5-(quinox- alin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Mt-3-PQPB) and 1-[3-(2H-1,3-benzodioxol-5-yl)-5- (quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one (Oxo-1,3-PQPB)) as a potential corrosion enhibitors in a mild hydrochloric acidic solution using 3 types of analysis techniques: electrochemical, spectroscopic as well as quantum chemical calculations. The results obtained showed that quinoxaline deravatives are very effective as corrosion inhibitors and their adsorption behaviour obeyed Langmuir adsorption isotherm.

Aoufir *et. al* [125] synthesized few quinoxaline deravatives (E)-3-(4-methoxystyryl)-7-methylquinoxalin-2(1H)-one (SMQ) and 2-(4-methoxyphenyl)-7-methyl-thieno[3,2-b] quinoxaline (TMQ). The synthesized compounds were screened for potential corrositon inhibition in an acidic solution under temperature of 303 K. the analysis techniques were carried out using electrochemical impedance spectroscopy and potentiodynamic polarization and the results obtained showed those synthesized quanoxaline deravatives to have good inhabitave properties for the corrosion of carbon steel in 1M HCl.

2.3 Pharmacological uses of quinoxaline derivatives

Carta *et al.* [22] reported the synthesis of thirty six novel series of 6 (7)- substituted-3-methyl or 3-halogenomethyl-2-phenylthio-phenylsulphonyl-chloro-quinoxaline 1,4-dioxides and also evaluated their for in vitro antimycobacterial, anticandida and antibacterial activities. The results obtained revealed that 3-methyl -2-phenylthioquinoxaline 1, 4-dioxides showed good activity against Micobacterium tuberculosis and exhibited MIC from 0.39 to 0.78 $\mu g\ mL^{-1}$. The antibacterial and anticandida activity results showed that the compounds 2,7-dichloro-3-methylquinoxaline 1,4-dioxide and 2-chloro-7-ethoxy-6-fluro-3-methylquinoxline, 1, 4-dioxide were the most active against Candida Krusei exhibiting MIC = 0.4 and 1.9 $\mu g\ mL^{-1}$ respectively.

Zarranz *et al.* [23] reported the synthesis of 2-alkylcarbonyl and 2-benzoyl-3-trifluromethyl quinoxaline 1,4-di-N-oxide derivatives and also investigated their for invitro antitumor activity against a 3-cell line panel which consisted of MCF7 (breast), NCI-H460 (lung), and SF-268 (CNS). The results obtained revealed that the anticancer activity depended on the substituents on the carbonyl group in the following increasing order; Ethyl < isopropyl < tertbutyl < phenyl –ones.These compounds are active and were found to inhibit the growth of all Leukemia cell lines. The most active compound was 2-benzoyl-6, 7-difluro-3-trifluromethylquinoxaline 1, 4-

di-N-oxide. The presence of two F-atoms in positions 6 and 7 and the benzoyl group in position 2 on a quinoxaline ring caused increased activity.

Barea *et al.* [24] reported the synthesis of 14 new 3-amino-1,4-di-N-oxide quinoxaline-2-carbonitrile derivatives. These new compounds were identified as active against malaria and leishmaniasis and they were evaluated for their in vitro antimalarial and antileishmanial activity against plasmodium falciparum Colombian FCR-3 strain and Leishmania amazonensis strain MHOM/BR/76/LTB-012 A. Graphic SAR and ADME properties were analysed further using computational studies. The investigation results indicated that these quinoxaline compounds with one halogenous group in position 6 and 7 provide an efficient activity against plasmodium and Leishmania parasite and show interesting ADME properties.

Khan *et al.* [68] studied three different steroidal thiazolo quinoxaline derivatives namely 3β-acetoxy-5α-cholestan-6-[thiozolo (4,5-b)quinoxaline-2-yl-hydrazone, 3β- chloro-cholestan-6-[thiozolo (4,5-b)quinoxaline-2-yl-hydrazene] and 5α-cholestan-6-[thiazolo (4,5-b)quinoxaline-2-yl-hydrazone prepared by the condensation reaction of steroidal thiosemicarbazones with 2,3-dichloroquinoxalines at 80^0C. They were evaluated for in vitro antibacterial activity against Escherichia coli using disk diffusion method and the investigation results were compared. Among all the three compounds, the compound 3β- chloro-cholestan-6-[thiozolo (4, 5-b) quinoxaline-2-yl-hydrazene] was found to be a better inhibitor of Escherichia coli.

Santivañez-Veliz *et.al* [126] synthesized 24 quinoxaline deravatives (1,4-di-N-oxide and two 1-N-oxide quinoxaline derivatives) and evaluated them for antimicobacterial activity using BacTiter-Glo microbial cell viability assay. Ten out of fifteen investigated compounds were found to be more active than the reference drugs, four of them stood out due to tocixity usually associated with the family of the coumpounds, lastly four out of the remaining five were found to be mutagenetic in both tested conditions.

Various quinoxaline derivatives were synthesized and evaluated for antimicrobial activity. Ganapaty *et al.* [127] synthesized some novel condensed bridgehead nitrogen heterocycles of quinoxalines and they were evaluated for antimicrobial activity against the gram-positive bacteria staphyllococus aureus and Bacillus subtilis, the gram-negative pseudomonas aeruginosa and proteus vulgaris, the fungi Aspergillus niger and the Mycobacterium tuberculosis $H_{37}Rv$ species.

3-benzyl-2-substituted quinoxaline was synthesized as novel monoamine oxidase A inhibitors by Hassan *et al.* [128] MAO inhibitors are used in neurological disorders such as parkinson's disease and depression. MAO-A inhibitors are used as antidepressant and antianxiety drugs.

Methyl [4-subtituted -2-quinoxalinyloxy) phenyl] acetates was synthesized by Sandra P [129] and evaluated for in vitro anti cancer activity by bioisosteric replacement.

3-phenyl-1-(1, 4-di-N-oxide quinoxaline-2-yl)-2-propene-1-one derivatives and their 4,5-dihydro-(1H)-pyrazole analogues were synthesized by Asuncion B [92]. The compounds were evaluated for anti-inflammatory and antioxidant activity. The tested compounds showed to exhibit the carrageenan-induced rat paw edema (4.5% - 56.1%).

Bailing Xu *et al.* [130] synthesized N4- (hetero) aryl sulfonyl quinoxalines and their analogs. The compounds were evaluated for anti viral activity as HIV-1 reverse transcriptase inhibitors. The ant-HIV-1 activities of compounds were evaluated by a cell-based HIV-1 replication pharmacological model which was set up by HIV-1 (pNL4-3) core packed with vesicular stomatitis virus glycoprotein.

CHAPTER 3

EXPERIMENTAL METHODS & THEORETICAL FRAMEWORK

3.1 EXPERIMENTAL METHODS

3.1.1. Chemicals and preparation of samples

All chemicals were used without any further purification. They were dried over 0.4 nm molecular sieves and under vacuum at ambient condition before they were used. Freshly degassed triply distilled water (specific conductance $>10^{-6}$ $S.cm^{-1}$) was used for the preparation of aqueous solution of quinoxaline derivatives. Ethanol and methyl acetate were purchased from Sigma Aldrich with purity of >99%.

The binary mixtures were prepared by transferring via syringe the pure liquids into stoppered bottles to prevent evaporation. The more volatile component was filled directly into the air-tight stoppard 10 cm^3 glass vial and then weighed. For the determination of mass of each component, OHAUS mass balance was used with precision of ± 0.0001 g. The uncertainty in molality was ± 0.0001 $mol \cdot kg^{-1}$. The mixture was shaken in order to ensure a complete homogeneity of the compounds. To avoid formation of bubbles inside the vibrating tube of the densitometer, sound velocity analyser, the injection was done slowly. Doubly distilled and deionised water was used for the preparation of the solutions. For the sake of comparison the density and sound velocity of the pure liquids (water, ethanol and methyl acetate) were measured and presented in Table 3.1 together with the available literature [131-142] showing good agreement with experimental data.

Table 3.1 Comparison of experimental density, q, and sound velocity, u of the pure liquids (water, ethanol and methyl acetate) with the corresponding literature values at T= (293.15, 298.15 303.15 and 308.15) K and at pressure p = 0.1 MPa.

Temperature (K)	Density ($kg.m^{-3}$)		Sound velocity ($m.s^{-1}$)	
	Exp.	Lit.	Exp.	Lit.
		Methyl acetate		
293.15	933.52		1177.3	
298.15	926.97	929.5[135] 0927.0[134]	1153.8	1167[135]
303.15	920.34	920.90[133]	1130.6	1132[133]
308.15	913.64	0.9164[135] 0.9150[136]	1106.0	
		Ethanol		
293.15	791.16	789.75[138]	1159.39	1162[138] 1146.3[140]
298.15	786.88	785.02[137] 758.46[138]	1142.75	1145[138]
303.15	782.56	781.15[138]	1125.85	1128[138]
308.15	778.20	776.41[139]	1109.01	
		Water		
293.15	998.29	998.26 [141]	1483.48	1482[131] 1482.7[141]
298.15	997.13	997.05 [138]	1497.78	1496 [132] 1497[138]
303.15	995.71	995.70 [141]	1510.17	1482.7 [141]
308.15	994.08	994.1[142]	1520.81	

In this work, density and sound velocity of twelve quinoxaline derivatives and their binary systems were determined at various temperatures and detailed specifications are presented in **Table 3.2.**

TABLE 3.2 Pure component specifications: Chemical name, suppliers, molecular weight, and mass percent purity for the quinoxaline derivatives used in the study.

SN	Compound	Abbreviation	Supplier	Molecular Weight ($g.mol^{-1}$)	Mass percent purity
		GROUP I			
1.	(N-{-3-[1-methanesulfonyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl] phenyl} methane sulphonamide	MQDPMS	Life Chemicals Inc.	445.52	>90
2.	N-{-2-[1-acetyl-5-(quinoxalin-5-yl)-4, 5-dihydropyrazol-3-yl] phenyl} methane sulphonamide,	AQDPMS	Vitas-M Laboratory, Ltd.	409.46	>90
3	N-{-2-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihdro-1H-pyrazol-3-yl] phenyl} methane sulfonamide	2PQDPMS	Vitas-M Laboratory, Ltd.	423.49	>90
4	N-{-3-[1-propanoyl-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-3-yl] phenyl} methane sulfonamide	3PQDPMS	Vitas-M Laboratory, Ltd.	423.49	>90
		GROUP II			
5	1-[3-(2H-1,3-benzodioxal-5-yl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one	BQDB	Molport	388.42	>90
6	1-[3-(3-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]propan-1-one,	3MQDP	Molport	360.41	>90
7	1-[3-phenyl-5-quinoxalin-6-yl-4,5-dihydropyrazol-1-yl]butan-1-one	3PQDB	Molport	344.41	>90
8	1-(3-(4-chlorophenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl) propan-1-one	4CQDPP	Molport	364.83	>90
		GROUP III			
9	2-phenyl-1-[[3-phenyl-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]ethanone	2PQDE	Molport	392.45	>97
10	1-(3-(4-methoxyphenyl)-5-(quinoxalin-6-yl)-4,5-dihydro-1H-pyrazol-1-yl)butan-1-one	4MQDPB	Molport	374.44	>98
11	2-ethyl-1-(5-(quinoxalin-6-yl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)butan-1-one	2EQDPB	Molport	386.49	>99
12	1-[3-(4-methylphenyl)-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-1-yl]butan-1-one	4MQDB	Molport	358.44	>99

3.1.2 Experimental methods for measurement of density and sound velocity

The prime object of density and sound velocity measurements in binary liquid systems is to estimate the value of isentropic compressibility (k_s), which cannot be done by any other method. Isentropic compressibility (k_s) has been widely used to study the molecular interactions through its excess value. It can also be used in fluid flow, mass flow and heat transfer processes in chemical industries.

The densities and sound velocities were measured using a digital vibrating-tube densimeter and sound velocity analyzer (Anton Paar DSA 5000M) with an accuracy of ± 0.02 K in temperature. The details of the experimental procedure can be found elsewhere [143-146]. The sensitivity of the instruments corresponds to a precision in density and sound velocity of $1x10^{-3}$ $kg.m^{-3}$ and $1x10^{-2}$ $m.s^{-1}$, respectively.

The instrument measured simultaneously density in the range of (0 to 3000) $kg.m^{-3}$ and sound velocity from (1000 to 2000) ms^{-1} at temperature range of (273.15 to 343.15) K with pressure variation from (0 to 0.3) MPa. The sound velocity was measured using a propagation time technique [147]. The standard uncertainty in measurements of density and sound velocity was ± 0.0008 $g{\cdot}cm^{-3}$ and ± 1.7 $m{\cdot}s^{-1}$, respectively. The reproducibility of results was confirmed by performing the measurements in triplicate. The sample was sandwiched between two piezo electric ultrasound transducers. One transducer emits sound waves through the sample- filled cavity (frequency around 3 MHz) and the second transducer received those waves. Thus, the sound velocity was obtained by dividing the known distance between transmitter and receiver by the measured propagation time of the sound waves. The detail procedure regarding the sound velocity measurement using the Anton Paar DSA 5000M is described by Fortin *et al.* [147].

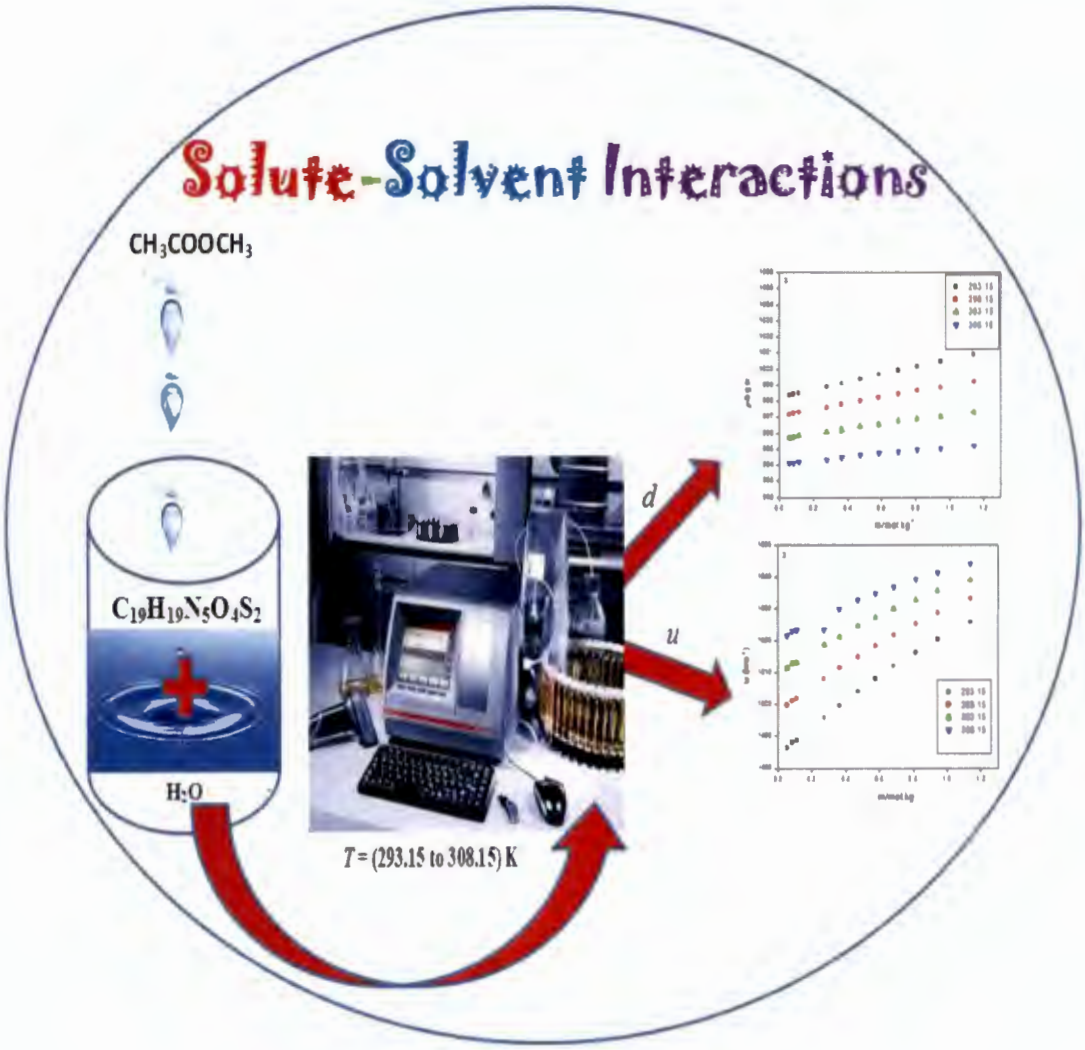


Fig 3.1 The graphical representation of the experimental work

Fig 3.2 Photograph of Density and Sound Velocity Meter (DSA 5000 M)

(Taken from Instruction Manual of Anton Paar DSA 5000 M)

Fig 3.3 Photograph of Density and Sound Velocity Meter (DSA 5000 M) fitted with X-sample 452.

(Taken from Instruction Manual of Anton Paar DSA 5000 M)

3.1.2.1 The oscillating U-tube method

The sample was introduced into a U-shaped borosilicate glass tube that is being excited to vibrate at its characteristic frequency. The frequency changes depending on the density of the sample. Through a precise determination of frequency, the density of the sample was measured using the following mathematical conversion. The density (ρ) was calculated from the quotient of the period of oscillations of the U-tube and the reference oscillator density.

$$\rho = KAxQ2xf1 - KBxf2 \qquad (3.1)$$

where KA, KB are apparatus constants.

Q2 is quotient of the period of oscillation of the U-tube divided by the period of oscillation of the reference oscillator.

f1, f2 are correction terms for temperature, viscosity and nonlinearity.

Figures 3.1, 3.2, and 3.3 shows the graphical representation of experimental work, DSA 5000 M and DSA 5000 M together with the RXA 156 and Xsample 452.

3.1.2.2 The sound velocity analyser

The sample was introduced into the sound velocity measuring cell which is attached by an ultrasonic transmitter on one side, by a receiver on the other side. The transmitter sent sound waves of a known period through the sample. The velocity of sound was calculated by determining of the period of received sound waves and the distance between the transmitter and receiver. Density and sound velocity are high temperature dependent properties. Therefore, the measuring cells have to be thermostated precisely.

3.1.2.3 Features and benefits of DSA 5000 M

The DSA 5000 M is the most developed instrument to measure density and sound velocity with highest precision with easy operation. The sample to be measured is usually filled manually by syringe.

DSA 5000 M instrument is equipped with the world's most advanced digital density and sound velocity measurement technology:

- By using optical pickups, the period of oscillation of the U-tube can be measured.
- Two integrated Pt 100 platinum thermometers together with Peltier elements provide very high precise thermostatting of the sample used.
- A Thermo balance is attached to DSA 5000 M which is used as an additional reference oscillator provides long-term stability and enables precise measurements. This arrangement makes it easy over the whole temperature range of the instrument with only one adjustment at 20 °C.
- Viscosity-related errors are automatically corrected by measuring the damping effect of the viscous sample followed by a mathematical correction of the density value.
- Special adjustments with standards of high viscosity and high density are provided in the instrument which leads to an enhanced precision for samples with high viscosity and high density.
- The sound velocity of the filled in sample can be determined accurately using an additional measuring cell made of stainless steel and high resolution electronics.

3.1.2.4 Error detection

- **Filling Check** The instrument detects inhomogeneities and gas bubbles automatically and generates a warning message in the density measuring cell by an advanced analysis of its oscillation pattern during measurement time
- **U-View** when using a density and sound velocity meter, the gas bubbles in the measuring cells are the major sources of errors. This issue was addressed by Anton paar by introducing a new feature-U-View. The U-tube in the measuring cell can be visually inspected for gas bubbles using a real time camera with zoom function.

3.1.2.5 Specifications of the DSA 5000 M

Specifications of the DSA 5000 M are given in **Table 3.3**

Table 3.3 Specifications of the DSA 5000 M

Measuring range sound velocity	1000 to 2000 m/s
Measuring range temperature	298.15 to 343.15K
Pressure range	0 to 3 bar
Required Sample volume per measurement approx.	3 ml
Measuring time per sample	1 to 4 min
Repeatability density	0.000001 g/cm^3
Repeatability sound velocity	0.1 m/s
Repeatability temperature	298.15 K
Ambient air pressure sensor	yes
Reference oscillator	yes
Automatic bubble detection	yes
Visual check of the density measuring cell	camera

3.1.2.6 Mittal ultrasonic interferometer

The instrument used for the measurement of sound velocity is Mittal ultrasonic interferometer M-81G. This simple and direct device determines the sound velocity in liquids with a high degree of accuracy.

3.1.2.6.1 Description

The ultrasonic interferometer consists of the following parts:

a) The high frequency generator: 1, 3. 5, & 10 MHz

b) The measuring cells: 1, 3, 5, & 10 MHz (one each)

c) Base to hold the cell.

d) Coax Cable

(a) The high frequency generator which is used to generate ultrasonic waves in the experimental liquid in the measuring cell. The high frequency generator induces ultrasonic waves by exciting the quartz plate fixed at the bottom of the measuring cell at its peak frequency thus producing ultrasonic waves in the liquid. A micro-ammeter senses the changes in the current and two controls for the sensitivity regulation and initial adjustments of the micro-ammeter are provided on the high frequency generator.

(b) The measuring cell is specially designed double walled cell for maintaining the temperature of the liquid constant during the experiment. A fine micrometre screw has been provided at the top which is used to raise or lower the reflector plate in the cell through a known distance. A quartz plate is fixed at the bottom.

3.1.2.6.2 Adjustments of ultrasonic interferometer

Two knobs are provided on high frequency generator for initial adjustment one is marked with "**ADJ**" to adjust the position of the needle on the ammeter and the knob marked "GAIN" is used to increase the sensitivity of the instrument for greater deflection.

The ammeter is used to notice the number of maximum deflections while the micrometre is moved up and down.

Fig 3.4 Photograph of the Mittal ultrasonic interferometer M-81G instrument.
(Taken from the Instruction Manual of Mittal enterprises ultrasonic interferometer)

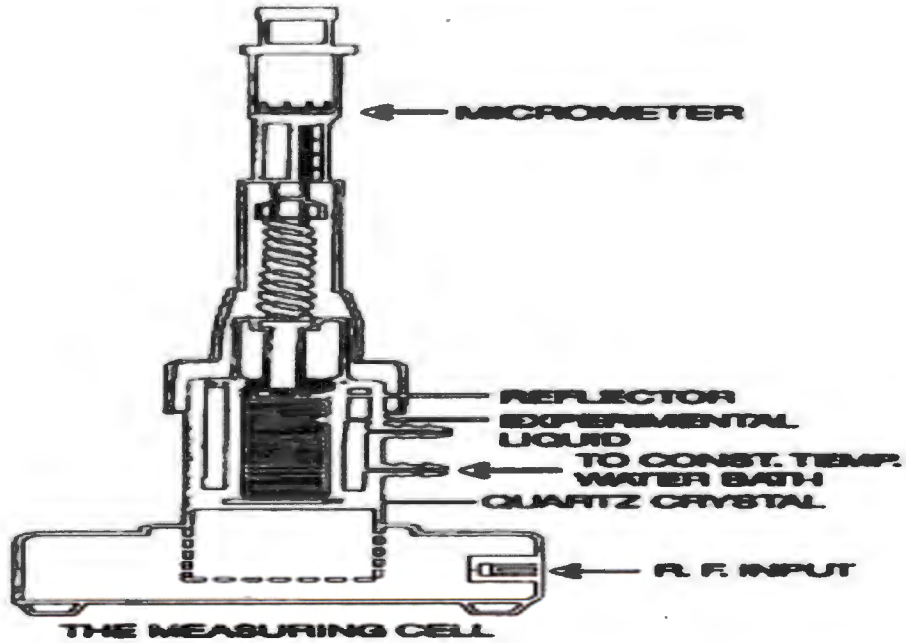


Fig 3.5 Photograph of interferometer.
(Taken from the Instruction Manual of Mittal enterprises ultrasonic interferometer)

3.1.2.6.3 Working principle

The principle used in the measurement of velocity (v), is based on the accurate measurement of the wavelength (λ) in the medium. The quartz plate fixed at the bottom of the cell produces ultrasonic waves of known frequency (γ). These waves are reflected by a movable metallic plate kept parallel to the quartz plate. If the separation between these two plates is exactly whole multiple of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz crystal and the anode current of the generator becomes maximum. If the distance between the reflector and crystal is increased or decreased and the variation is one half wave length, or multiple of it, the anode current again becomes maximum.

Using the wavelength (λ), the sound velocity (v) can be calculated by the following relation:

Velocity = Wavelength x Frequency

$$v = \lambda \times \gamma \tag{3.2}$$

3.1.2.6.4 Technical specifications

1) High frequency generator

Mains Voltage	220v, 50Hz
Measuring frequency	1, 3, 5, & 10 MHz
Fuse	500 mA
Weight	3.5Kg approximately.

2) Measuring cell

Maximum displacement of the reflector	20 mm
Required quantity of liquid	10 c.c
Least Count of micrometre	0.001 mm
Weight	3.75 Kg approximately.

3) Shielded cable

Length of connecting cable between the generator and the cell is 50 cm approximately.

3.2 THEORETICAL FRAMEWORK

3.2.1 Density and sound velocity

Densities are highly temperature dependent values. Density, (ρ), of a sample is defined as the mass (m), divided by the volume (v), of the sample.

$$\rho = \frac{m}{v} \tag{3.3}$$

The sound velocity is an important property during the study of binary mixture. It is very much useful to derive some thermophysical property like isentropic compressibility, isobaric thermal expansion coefficient, heat capacities. These derived properties are so important in design and optimization of a number of chemical processes [146].

3.2.2. Theories of sound velocity

The following theories are used for the prediction of ultrasonic velocity in the binary liquid mixtures.

3.2.2.1 Nomoto's Relation (U_{NR})

On assuming the additivity of molar sound velocity (R) and no volume change on mixing, Nomoto [148,149] established the following relation for the ultrasonic velocity of binary liquid mixtures:

$$R = \frac{M}{\rho U^{1/2}} \tag{3.4}$$

where ρ and U are densities and sound velocities which are experimentally determined values and M is the mean molecular weight in a binary liquid mixture:

$$M = X_1M_1 + X_2M_2 \tag{3.5}$$

where M_1 and M_2 are molecular weights and x_1 and x_2 are mole fractions of constituent components. Simple arrangement yields the Nomoto's relation as follows.

$$U_{NR} = \left(\frac{X_1 R_1 + X_2 R_2}{X_1 V_1 + X_2 V_2}\right)^3 \quad (3.6)$$

3.2.2.2. Ideal mixture relation (U_{IMR})

Van Deal and Vangeel (1969) [150] suggested the following relation for the velocity of sound

$$U_{IMR} = \left[\frac{1}{X_1 m_1 + X_2 m_2}\right]^{1/2} \left[\frac{X_1}{m_1 U_1^2} + \frac{X_2}{m_2 U_2^2}\right]^{-1/2} \quad (3.7)$$

where u_1 and u_2 are the velocities of the individual components.

3.2.2.3. Junjie's method (U_{JM})

Junjie's equation is given as:

$$U_{JM} = \left[\frac{X_1 V_1 + X_2 V_2}{(X_1 m_1 + X_2 m_2)^{1/2}}\right] \left[\frac{X_1 V_1}{d_1 U_1^2} + \frac{X_2 V_2}{d_2 U_2^2}\right]^{-1/2} \quad (3.8)$$

where M_1, M_2 are molecular weights of constituent components, d_1 and d_2 are densities of constituent components.

3.2.2.4. Impedance Relation (U_{IMR})

Impedance is the product of ultrasonic velocity (U) and the density (ρ) of a liquid mixture. Hence the impedance relation predicts the ultrasonic velocity of the given mixture by using the values of impedance (Z_i) and the density (ρ) values. Impedance relation is given as $U_{IR} = \frac{\sum X_i Z_i}{\sum X_i \rho_i}$ (3.9)

where X_i, Z_i, ρ_i are the mole fraction, acoustic impedance and density of the mixture respectively.

3.2.2.5 Rao's specific velocity method is given as

$$U_R = (\Sigma x_i r_i \rho_i)^3 \quad (3.10)$$

where x_i is the mole fraction, U_i is the ultrasonic velocity and ρ_i is the density of a mixture, r_i is the Rao's specific sound velocity, which is given by:

$r_i = \frac{u_i^{\frac{1}{3}}}{\rho_i}$ and Z_i is the acoustic impedance. (3.11)

3.2.2.6. Free length theory (FLT)

In recent years many attempts have been made [151-153] to study molecular interactions in pure and binary liquid mixtures. Among the various theories taken into consideration for non-polar type of mixtures Free Length Theory is found to yield excellent comparison with the experimental values.

Jacobson introduced the concept of intermolecular free length to determine the ultrasonic velocity in pure liquids and liquid mixtures. For liquid mixtures

$$U_{FLT} = \frac{K_T}{L_f \rho^{\frac{1}{2}}} \quad (3.12)$$

where K_T is the temperature dependent Jacobson constant which takes a value of 199.976 x 10^{-8} at 303K. L_f is the free length in the liquid and ρ is the density. The free length theory of Jacobson [154], was used by many investigators [155-159] to evaluate the sound velocities in the liquid mixture. But they arrived with a conclusion that the FLT produces large deviation with experimental values. In a mixture,

$$u_{mix} L_{mix} \rho_{mix}^{\frac{1}{2}} = K \quad (3.13)$$

where u_{mix}, ρ_{mix} L_{mix} are sound velocity, density, and free length in the mixture. Free length (L_f) of pure liquids is calculated using the relation:

$$L_f = \frac{K}{u_{exp}\rho_{exp}^{\frac{1}{2}}} \tag{3.14}$$

where u_{exp}, ρ_{exp} are experimentally determined sound velocity and density, respectively. The surface area Y, per mole for the pure component is obtained using the following expression:

$$Y = \frac{2V_a}{L_f} \tag{3.15}$$

where $V_a = V_T - V_0$, (3.16)

where V_a is the available volume per mole, and V_0 and V_T are molar volumes at absolute zero and at absolute temperature T, respectively. The values of V_0 can be obtained using critical temperature as follows

$$V_0 = V_T\left(1 - \frac{T}{T_c}\right)^{0.3} \tag{3.17}$$

L_{mix} is calculated using the following expression:

$$L_{mix} = \frac{2\left[V - \sum_{i=1}^{3} x_i V_0^i\right]}{\sum_{i=1}^{3} x_i y_i} \tag{3.18}$$

where x_i and V_0^i denote mole fraction and molar volume at absolute Zero of component i, respectively and V represents molar volume of mixture.

3.2.2.7. Schaaff's Collision Factor Theory (CFT)

On the basis of molecular kinetic theory, Schaaffs [160], developed the following formula for sound velocity in pure liquids.

$$U = U_{\infty} S r_f = \frac{U_{\infty} SB}{V} \tag{3.19}$$

where U_{∞} = 1600 ms^{-1}, S is the collision factor, $r_f = \frac{B}{V}$ is the space filling factor, B is the actual volume of the molecules per mole of the liquid and V is the molar volume. Nutsch Kuknkies [161], extended this concept to the binary mixtures and showed the following relation as:

$$U_{mix} = U_{\infty} S_{mix} r_{f(mix)} \tag{3.20}$$

This can be written as:

$$U_{mix} = U_{\infty} \left[\frac{(x_1 B_1 + x_2 B_2)(x_1 S_1 + x_2 S_2)}{(x_1 v_1 + x_2 v_2)} \right] \tag{3.21}$$

The suffixes 1, and 2 denote the components 1, and 2, respectively. The values of B for the pure components can be obtained using eqn (3.32).

$$B = \frac{4\Pi}{3} r_m^3 N \tag{3.22}$$

where r_m is the molecular radius and N is the Avogadro's number. The value of r_m can be obtained from Schaaff's semi empirical formula and the expression suggested by Gopala and Venkataseshaiah [162].

CHAPTER 4
RESULTS & DISCUSSION

4.1 GROUP 1: MQDPMS, AQDPMS, 2PQDPMS, 3PQDPMS

4.1.1 Density and sound velocity measurements

The densities, *d*, sound velocity, *u*, were measured at T= 293.15, 298.15, 303.15 and 308.15 K and at pressure p = 0.1 Mpa and the values are presented in **Table 4.1.1.**

4.1.2. Apparent molar quantities

The apparent molar volume, V_φ, and apparent molar adiabatic compressibility, k_φ, were calculated using the experimental density and sound velocity values by using the following equations (4.1) and (4.2),

$$V_\varphi = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m\rho\rho_0} \tag{4.1}$$

$$k_\varphi = \frac{(k_S\rho_0 - k_{S0}\rho)}{m\rho\rho_0} + \frac{k_S M}{\rho} \tag{4.2}$$

where m is the molality (mol·kg^{-1}) of methyl acetates in aqueous solutions of MQDPMS, AQDPMS, 2PQDPMS or 3PQDPMS, M is the molar mass of the solute (methyl acetate) (kg·mol^{-1}) and ρ_0 and ρ are the densities (kg·m^{-3}) and $k_{S\,0}$, and k_S are the coefficient of adiabatic compressibility (Pa^{-1}) of reference solvent (desired molality of aqueous MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS and (methyl acetate + MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS + water) ternary mixtures, respectively and u is the sound velocity of the mixture. The resulting values of V_φ and k_φ for the mixture of methyl acetate in aqueous solution of MQDPMS, AQDPMS, 2PQDPMS or 3PQDPMS at 293.15, 298.15, 303.15 and 308.15 K are also been presented in **Table 4.1.1**.

Table 4.1.1 Densities (d), sound velocity (u), apparent molar volumes (V_φ), and apparent molar adiabatic compressibility (k_φ), of methyl acetate in aqueous solution of MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS at T= (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 Mpa.

m (mol·kg^{-1})	d (kg·m^{-3})	u (m·s^{-1})	$10^6 \cdot V_\varphi$ (m^3·mol^{-1})	$10^6 \cdot k_\varphi$ (m^3·mol^{-1}·Pa^{-1})
Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} MQDPMS				
		T = 293.15 K		
0.0553	998.41	1486.3	-1.18	8240.5
0.0842	998.54	1488.0	-0.75	5411.2
0.1119	998.59	1488.8	-0.55	4076.9
0.2740	998.92	1495.8	-0.18	1667.7
0.3642	999.14	1499.6	-0.12	1255.9
0.4729	999.41	1504.0	-0.07	968.7
0.5783	999.66	1508.0	-0.05	793.5
0.6859	999.92	1512.0	-0.03	670.2
0.8173	1000.21	1516.2	-0.01	564.2
0.9473	1000.51	1520.4	0.00	488.2
1.1405	1000.94	1525.7	0.01	407.7
		T = 298.15 K		
0.0553	997.21	1499.8	-1.30	8112.2
0.0842	997.32	1501.2	-0.83	5328.9
0.1119	997.38	1501.9	-0.60	4015.6
0.2740	997.64	1508.0	-0.20	1645.2
0.3642	997.82	1511.3	-0.14	1240.0
0.4729	998.04	1515.0	-0.09	957.4
0.5783	998.24	1518.4	-0.06	785.0
0.6859	998.45	1521.7	-0.04	663.7
0.8173	998.68	1525.2	-0.02	559.3
0.9473	998.91	1528.7	-0.01	484.5
1.1405	999.25	1533.0	0.01	405.2
		T = 303.15 K		
0.0553	995.78	1511.6	-1.41	8008.4
0.0842	995.86	1512.9	-0.90	5262.4
0.1119	995.94	1513.4	-0.66	3966.3
0.2740	996.12	1518.6	-0.23	1627.2
0.3642	996.26	1521.3	-0.15	1227.4
0.4729	996.43	1524.5	-0.10	948.6
0.5783	996.59	1527.3	-0.07	778.5
0.6859	996.75	1530.0	-0.05	658.7
0.8173	996.92	1532.9	-0.03	555.7
0.9473	997.09	1535.6	-0.01	481.9
1.1405	997.34	1539.0	0.00	403.6
		T = 308.15 K		
0.0553	994.13	1521.8	-1.52	7927.7

0.0842	994.19	1522.9	-0.98	5210.9
0.1119	994.19	1523.3	-0.72	3928.1
0.2740	994.28	1523.3	-0.25	1623.4
0.3642	994.49	1529.9	-0.17	1218.1
0.4729	994.62	1532.5	-0.11	942.1
0.5783	994.73	1534.7	-0.08	773.8
0.6859	994.85	1536.9	-0.06	655.3
0.8173	994.96	1539.1	-0.03	553.3
0.9473	995.08	1541.3	-0.02	480.3
1.1405	995.23	1543.8	0.00	402.8
0.9472	997.06	1510.9	-0.01	482.7
1.1405	997.30	1511.7	0.00	401.6
Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} AQDPMS				
		***T* = 293.15 K**		
0.0556	998.35	1485.3	-1.17	8208.5
0.0798	998.40	1486.5	-0.80	5720.7
0.1144	998.49	1488.1	-0.53	3992.7
0.3054	998.94	1496.4	-0.16	1498.8
0.3660	999.09	1498.9	-0.12	1251.4
0.4711	999.35	1503.2	-0.08	973.4
0.5784	999.60	1507.3	-0.05	794.3
0.6914	999.87	1511.4	-0.03	665.7
0.8169	1000.17	1515.7	-0.01	564.9
0.9462	1000.46	1519.7	0.00	489.2
1.1470	1000.89	1525.5	0.01	405.8
		***T* = 298.15 K**		
0.0556	997.16	1499,9	-1.29	8079.6
0.0798	997.20	1501.3	-0.88	5632.3
0.1144	997.28	1508.5	-0.59	3932.2
0.3054	997.65	1510.7	-0.18	1478.7
0.3660	997.77	1514.3	-0.13	1235.3
0.4711	997.98	1517.7	-0.09	961.8
0.5784	998.19	1521.2	-0.06	785.6
0.6914	998.41	1524.8	-0.04	659.1
0.8169	998.64	1528.1	-0.02	559.9
0.9462	998.87	1532.8	-0.01	485.4
1.1470	999.20	1510.9	0.01	403.3
		***T* = 303.15 K**		
0.0556	995.73	1512.9	-1.40	7974.7
0.0798	995.77	1519.0	-0.96	5560.5
0.1144	995.83	1520.8	-0.64	3883.4
0.3054	996.13	1523.9	-0.20	1462.7
0.3660	996.22	1526.7	-0.15	1222.6
0.4711	996.39	1529.6	-0.10	952.8
0.5784	996.55	1532.5	-0.07	778.9
0.6914	996.71	1535.2	-0.05	654.1
0.8169	996.89	1538.8	-0.03	556.2
0.9462	997.06	1510.9	-0.01	482.7
1.1470	997.30	1511.7	0.00	401.6

		$T = 308.15$ K		
0.0556	994.09	1521.9	-1.52	7892.3
0.0798	994.12	1522.9	-1.03	5504.4
0.1144	994.16	1528.0	-0.70	3845.5
0.3054	994.39	1529.5	-0.22	1450.7
0.3660	994.46	1532.0	-0.17	1213.1
0.4711	994.58	1534.3	-0.11	946.2
0.5784	994.70	1536.6	-0.08	774.1
0.6914	994.82	1538.9	-0.05	650.7
0.8169	994.94	1541.0	-0.03	553.8
0.9462	995.05	1543.6	-0.02	481.0
1.1470	995.21	1521.3	0.00	400.8
Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 2PQDPMS				
		$T = 293.15$ K		
0.0621	998.35	1483.7	-1.04	7344.5
0.0935	998.43	1485.5	-0.67	4882.8
0.1126	998.47	1486.6	-0.54	4055.7
0.2747	998.86	1488.0	-0.18	1665.3
0.3605	999.06	1495.1	-0.12	1270.2
0.4685	999.37	1498.9	-0.08	978.0
0.5796	999.60	1503.4	-0.05	792.6
0.6869	999.85	1507.6	-0.03	670.1
0.8077	1000.13	1511.7	-0.01	571.3
0.9463	1000.45	1515.4	0.00	489.2
1.1428	1000.87	1519.7	0.01	407.3
		$T = 298.15$ K		
0.0621	997.16	1496.6	-1.15	7229.9
0.0935	997.23	1499.0	-0.74	4807.7
0.1126	997.26	1500.1	-0.60	3994.2
0.2747	997.59	1501.2	-0.20	1642.5
0.3605	997.75	1507.4	-0.14	1253.8
0.4685	998.00	1510.7	-0.09	966.4
0.5796	998.19	1514.4	-0.06	784.0
0.6869	998.39	1518.0	-0.04	663.4
0.8077	998.62	1521.5	-0.02	566.2
0.9463	998.86	1524.6	-0.01	485.4
1.1428	999.19	1528.1	0.01	404.7
		$T = 303.15$ K		
0.0621	995.73	1508.9	-1.25	7136.8
0.0935	995.78	1511.0	-0.80	4746.9
0.1126	995.81	1511.9	-0.66	3944.5
0.2747	996.07	1512.9	-0.23	1624.3
0.3605	996.20	1518.1	-0.15	1240.8
0.4685	996.40	1520.9	-0.10	957.5
0.5796	996.54	1524.0	-0.07	777.3
0.6869	996.70	1527.0	-0.05	658.4
0.8077	996.87	1529.8	-0.03	562.4
0.9463	997.06	1532.3	-0.01	482.7
1.1428	997.29	1535.2	0.00	403.1

		T = 308.15 K		
0.0621	994.08	1519.5	-1.35	7064.2
0.0935	994.13	1521.3	-0.87	4699.8
0.1126	994.15	1522.0	-0.71	3905.9
0.2747	994.35	1522.9	-0.25	1610.6
0.3605	994.45	1527.2	-0.17	1231.1
0.4685	994.59	1529.5	-0.12	950.9
0.5796	994.69	1532.1	-0.08	772.5
0.6869	994.81	1534.5	-0.06	654.9
0.8077	994.93	1536.8	-0.04	559.9
0.9463	995.05	1538.7	-0.02	481.0
1.1428	995.20	1540.9	0.00	402.2
	Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 3PQDPMS			
		T = 293.15 K		
0.0582	998.43	1485.5	-0.75	5445.6
0.0838	998.50	1486.6	-0.54	4026.4
0.1134	998.88	1488.0	-0.18	1643.4
0.2784	999.11	1495.1	-0.12	1250.1
0.3663	999.37	1498.9	-0.07	965.6
0.4749	999.65	1503.4	-0.05	786.0
0.5844	999.91	1507.6	-0.03	658.0
0.6996	1000.16	1511.7	-0.01	569.5
0.8102	1000.47	1515.4	0.00	487.7
0.9494	1000.89	1496.6	0.01	406.9
		T = 298.15 K		
0.0582	997.23	1500.1	-0.83	5361.5
0.0838	997.29	1501.2	-0.60	3965.4
0.1134	997.61	1507.4	-0.20	1620.8
0.2784	997.79	1510.7	-0.13	1234.0
0.3663	998.01	1514.4	-0.09	954.1
0.4749	998.23	1518.0	-0.06	777.4
0.5844	998.44	1521.5	-0.04	651.5
0.6996	998.64	1524.6	-0.02	564.4
0.8102	998.88	1528.1	-0.01	483.9
0.9494	999.21	1532.6	0.01	404.4
		T = 303.15 K		
0.0582	995.79	1511.0	-0.91	5293.4
0.0838	995.84	1511.9	-0.65	3916.0
0.1134	996.09	1512.9	-0.22	1602.9
0.2784	996.24	1518.1	-0.15	1221.3
0.3663	996.41	1520.9	-0.10	945.2
0.4749	996.58	1524.0	-0.07	770.9
0.5844	996.74	1527.0	-0.04	646.6
0.6996	996.89	1529.8	-0.03	560.7
0.8102	997.08	1532.3	-0.01	481.2
0.9494	997.31	1535.2	0.00	402.7
		T = 308.15 K		
0.0582	994.14	1521.3	-0.98	5240.4
0.0838	994.18	1522.0	-0.71	3877.8
0.1134	994.37	1522.9	-0.24	1589.3

0.2784	994.48	1527.2	-0.17	1211.8
0.3663	994.60	1529.5	-0.11	938.7
0.4749	994.73	1532.1	-0.08	766.2
0.5844	994.84	1534.5	-0.05	643.2
0.6996	994.95	1536.8	-0.04	558.2
0.8102	995.07	1538.7	-0.02	479.5
0.9494	995.22	1540.9	0.00	401.9

The values of *d* and *u,* for methyl acetate in 0.0006, 0.0006, 0.0005 and 0.0005, $mol.kg^{-1}$ aqueous solution of MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS, respectively, against the modalities of methyl acetate at different temperatures are presented in **Figures 4.1.1. (a-d) and 4.1.2(a-d).**

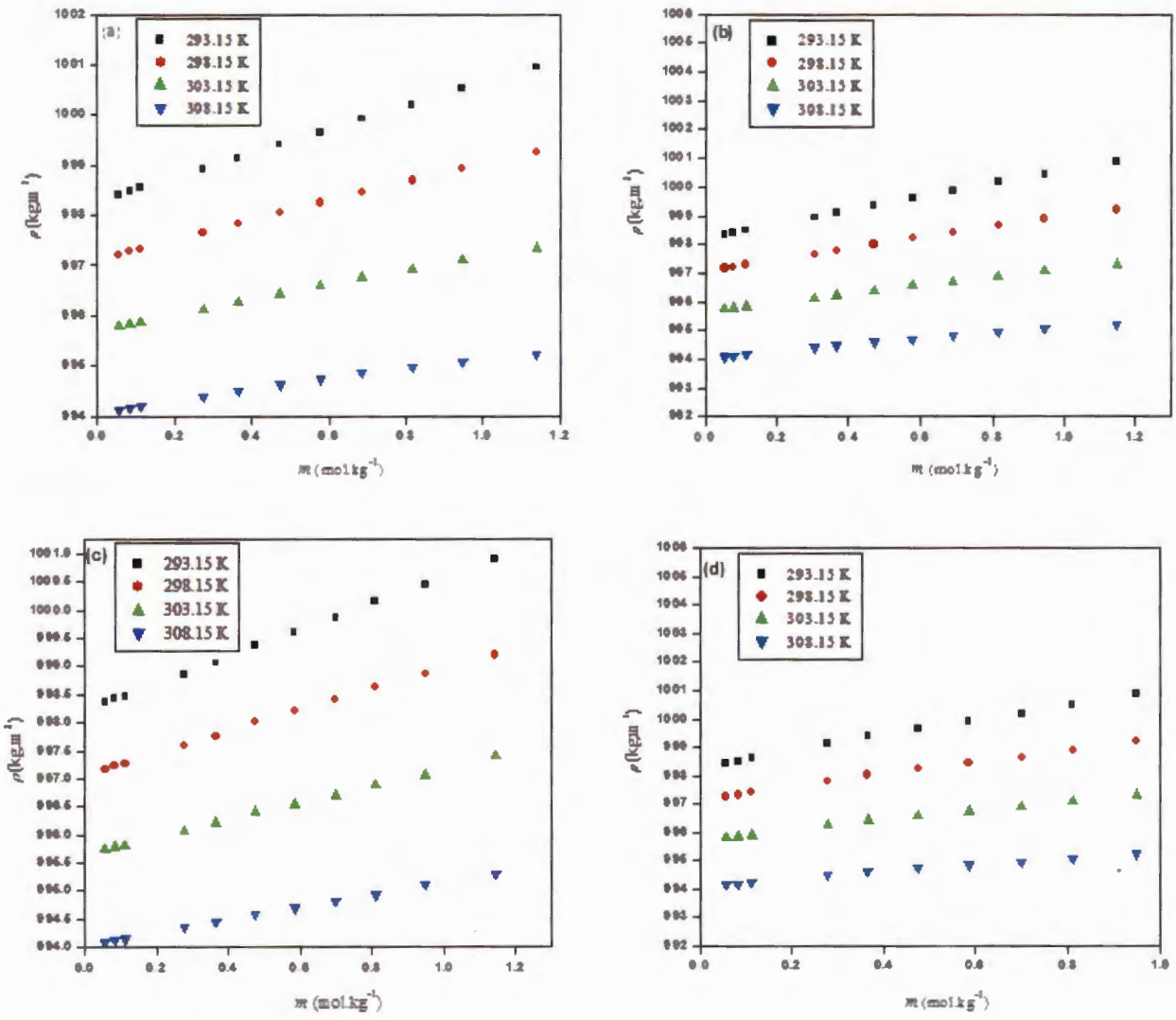


Fig. 4.1.1 Density, ρ, for the mixture of methyl acetate in aqueous solution of (a) MQDPMS, (b) AQDPMS, (c) 2PQDPMS, and (d) 3PQDPMS at 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

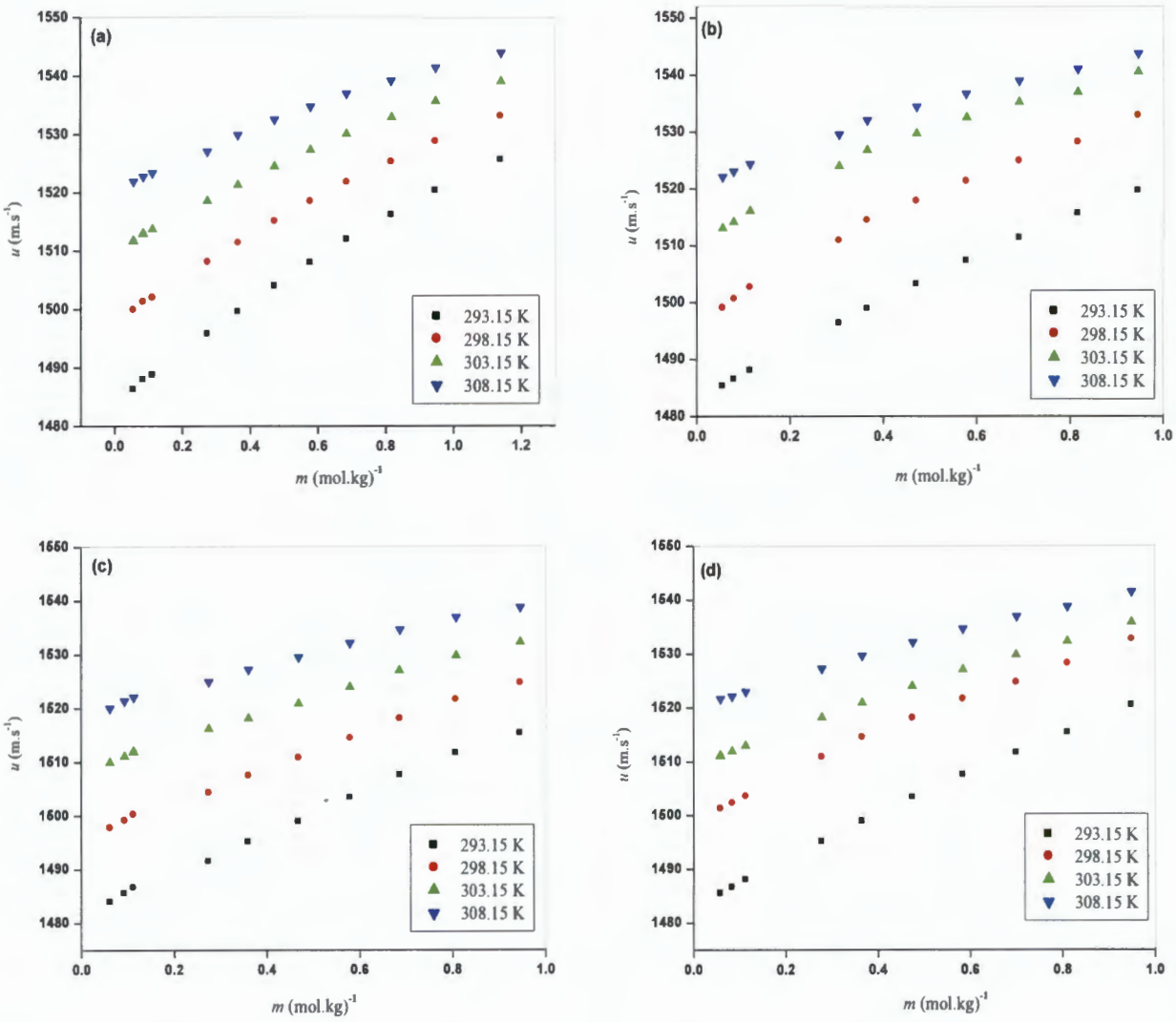


Fig. 4.1.2. Sound velocity, u, for the mixture of methyl acetate in aqueous solution of (a) MQDPMS, (b) AQDPMS, (c) 2PQDPMS, and (d) 3PQDPMS at 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

From **Figures 4.1.1 (a-d)** and **4.1.2 (a-d),** it can be observed that the values of density, (*d*) increased with an increase in concentration and decreased with temperature while the values of sound velocity (*u*) increased with both temperature and concentration. The increase in the values of density is due to the presence of strong intermolecular attraction such as solute-solvent attraction. An increase in concentration allows for a closer approach of solvent and solute molecules, and stronger association between solute and solvent molecules [163]. The sound velocity values increases or decreases depending on solute structure and their properties. In this investigation of group I compounds, methyl acetate which is a solute increased the sound velocity values and therefore acts as a structure maker [163]. The density and sound velocity values of the studied mixtures are not exactly the same but show very slight variations due to the nature of quinoxaline derivatives studied. 2PQDPMS and 3PQDPMS have same molar mass but change in position in structure, MQDPMS and AQDPMS have similar structure with acetyl (A) and methanesulfonyl group but all of them have QDPMS group which results in very slight variations on density and sound velocity data of studied mixtures.

The value of v_φ and $k\varphi$ for methyl acetate in 0.0006, 0.0006, 0.0005 and 0.0005, mol.kg^{-1} in aqueous solution of MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS, respectively, against the modalities of methyl acetate at different temperature have also been plotted in **Figures 4.1.3 (a-d)** and **4.1.4 (a-d),** respectively.

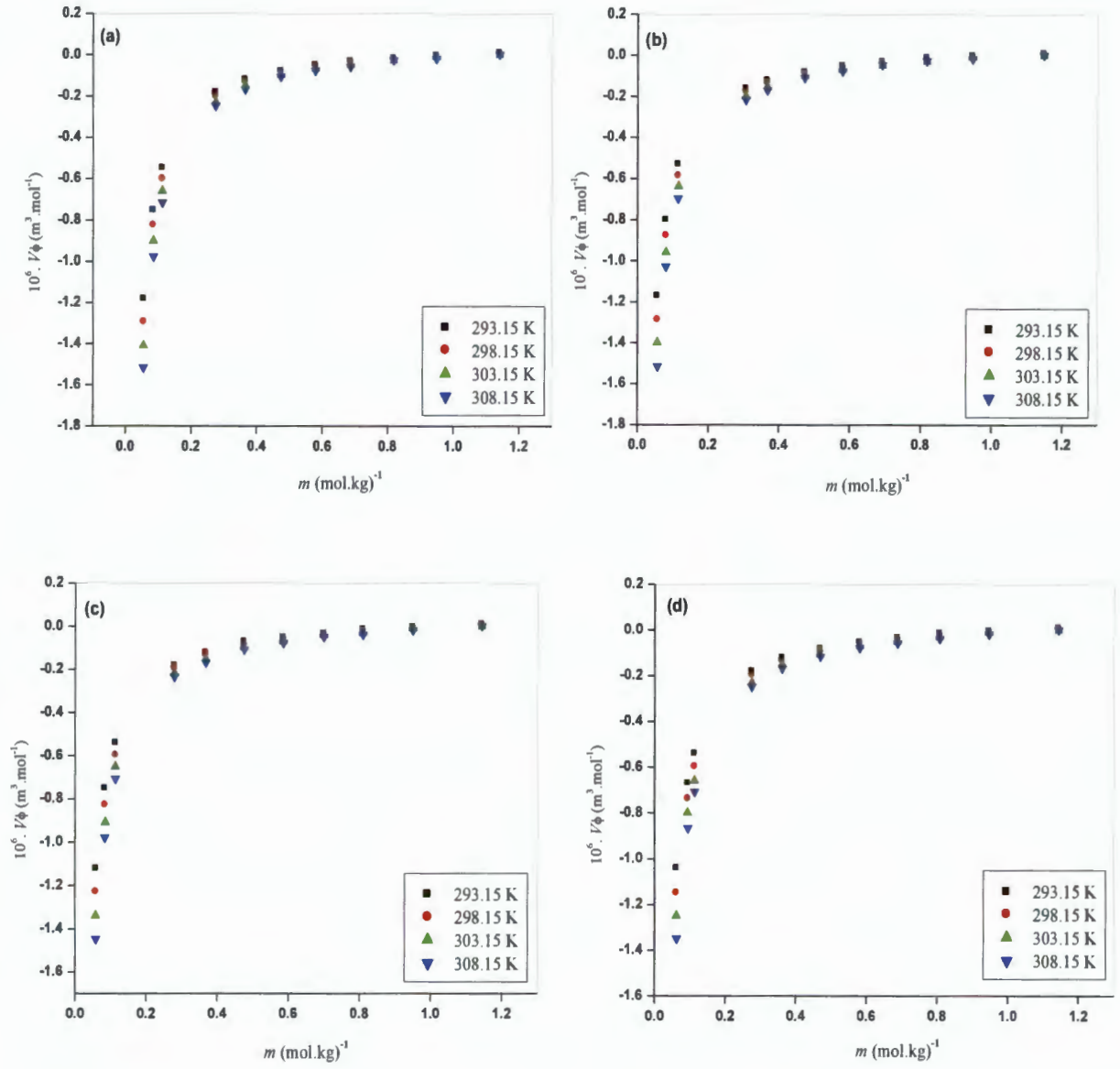


Fig. 4.1.3 Apparent molar volume, V_φ, for the mixture of methyl acetate in aqueous solution of (a) MQDPMS, (b) AQDPMS, (c) 2PQDPMS, and (d) 3PQDPMS at 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

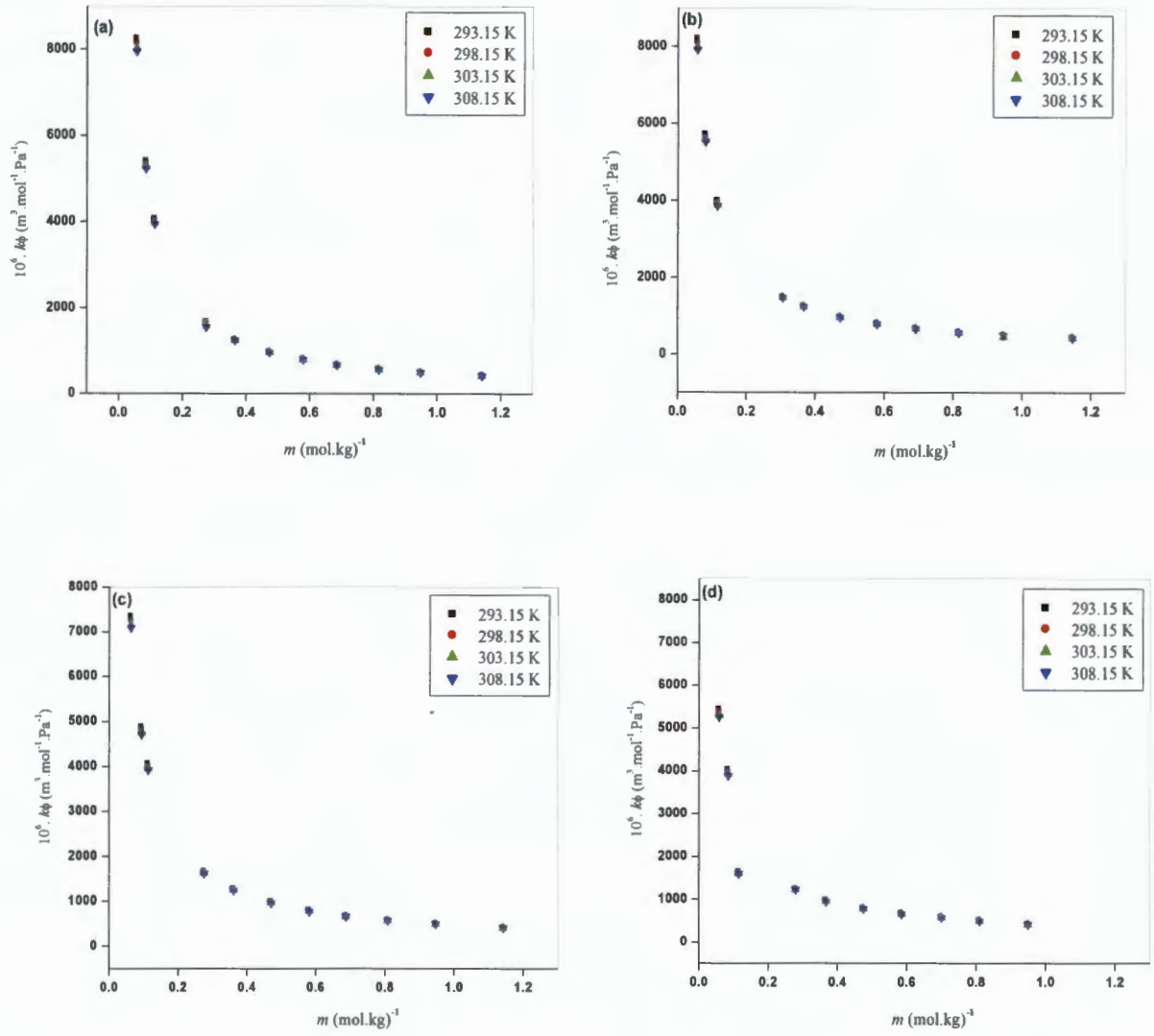


Fig. 4.1.4 Apparent molar adiabatic compressibility, k_φ, for the mixture of methyl acetate in aqueous solution of (a) MQDPMS, (b) AQDPMS, (c) 2PQDPMS, and (d) 3PQDPMS at 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

Figure 4.1.3 (a-d), shows that the apparent molar volume decreases with an increase in temperature for all the systems. The apparent molar volumes are negative but only few are positive at higher concentration for all systems and increase with an increase in concentration for all the systems. Increasing values of V_φ with concentration of solute were observed in the (methanol + methyl acetate) system [164]. For all the systems low molality of solute, the solute are surrounded by solvent molecules indicating strong (solute-solvent) interactions and increasing the solute concentration the (solute-solute) interaction increases resulting in large V_φ values. The V_φ values are negative and increase with concentration which suggests that the overall structural order is reduced in solution. The $V\varphi$ values are positive at higher concentration which suggests that the overall structural order is enhanced in solution at higher concentration of methyl acetate [165].

Figure 4.1.4 (a-d), shows that the apparent molar adiabatic compressibility (k_φ) values decreases with an increase in temperature for all the systems. These plots also show that at a fixed temperature, k_φ values decreases with an increase in concentration of the solute for all the systems. The kφ values are positive for all the systems which indicate that methyl acetate rich region is more compressible as compared with bulk solution [166]. The positive $k\varphi$ values are attributed to the weak interactions between the solute and solvent.

4.1.3. Apparent molar quantities at infinite dilution

The variation of apparent molar volume V_φ and apparent molar adiabatic compressibility $k\varphi$ with the concentration can be adequately represented by the equations (4.3) and (4.4)

$$V_\varphi = V_\varphi^0 + S_V m^{1/2} + B_V m \qquad (4.3)$$

$$k_\varphi = k_\varphi^0 + S_k m^{1/2} + B_k m \qquad (4.4)$$

where V_φ^0 and k_φ^0 are the limiting values of apparent molar volume and apparent adiabatic compressibility, respectively and are often regarded equal to the infinite dilution partial molar volume and infinite dilution partial molar adiabatic compressibility. The terms S_V, B_V, S_k and B_k represent the values of the experimental slopes which provide significant information regarding the intermolecular interactions that exist in solution. The values of V_φ^0, k_φ^0 S_V, B_V, S_k, B_k and standard errors (derived by least-squares fitting of V_φ and k_φ values to equations 4.3 and 4.4) are presented in **Tables 4.1.2 and 4.1.3.**

Table 4.1.2 Limiting apparent molar volumes (V_φ^0) and fitting parameters S_V and B_V, of methyl acetate in, aqueous solution of MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS at T= (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 Mpa.

T/K	10^6X V_φ^0 ($m^3 \cdot mol^{-1}$)	10^6X S_V ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$)	10^6X B_V ($m^3 \cdot mol^{-2} \cdot kg$)	10^6X σ
Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} MQDPMS				
293.15	-1.91	4.51	-2.62	0.10
298.15	-2.09	4.92	-2.85	0.12
303.15	-2.27	5.33	-3.09	0.12
308.15	-2.45	5.74	-3.32	0.13
Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} AQDPMS				
293.15	-1.91	4.46	-2.56	0.10
298.15	-2.09	4.90	-2.82	0.11
303.15	-2.27	5.31	-3.06	0.12
308.15	-2.46	5.73	-3.30	0.13
Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 2PQDPMS				
293.15	-1.28	3.24	-2.03	0.11
298.15	-1.40	3.54	-2.22	0.12
303.15	-1.53	3.87	-2.43	0.13
308.15	-1.65	4.15	-2.60	0.14
Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 3PQDPMS				
293.15	-1.76	4.09	-2.34	0.09
298.15	-1.94	4.49	-2.57	0.10
303.15	-2.10	4.88	-2.79	0.10
308.15	-2.26	5.21	-2.98	0.11

Table 4.1.3 Limiting apparent molar adiabatic compressibility (k_{φ}^{0}), and fitting parameters S_K and B_K, of methyl acetate in aqueous solution of MQDPMS or AQDPMS or 2PQDPMS or 3PQDPMS at T= (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 Mpa.

T/K	$10^6\ k_{\varphi}^{0}$ ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)	$10^6\ S_K$ ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2} \cdot Pa^{-1}$)	$10^6\ B_K$ ($m^3 \cdot mol^{-2} \cdot kg \cdot Pa^{-1}$)	$10^6 X\ \sigma$
	Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} MQDPMS			
293.15	13013.7	-29646.9	17191.6	0.9
298.15	12808.8	-29169.9	16914.7	0.9
303.15	12642.9	-28783.2	16690.3	0.9
308.15	12511.0	-28464.6	16500.8	0.9
	Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} AQDPMS			
293.15	13060.9	-29568.9	17044.6	0.9
298.15	12853.4	-29089.5	16768.1	0.9
303.15	12684.3	-28697.6	16541.9	0.9
308.15	12551.3	-28388.0	16363.1	0.9
	Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 2PQDPMS			
293.15	13534.2	-32496.8	20068.2	0.9
298.15	13319.1	-31970.7	19743.4	0.9
303.15	13143.9	-31540.7	19477.7	0.9
308.15	13007.0	-31203.3	19269.1	0.9
	Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 3PQDPMS			
293.15	12093.3	-27083.6	15522.4	0.9
298.15	11901.5	-26644.4	15270.5	0.9
303.15	11745.5	-26286.4	15065.2	0.9
308.15	11623.6	-26005.2	14903.8	0.9

Table 4.1.2 shows that V_{φ}^{0} values are negative and decrease with an increase in temperature for all systems. This indicates the presence of week solute-solvent interactions and these interactions decreases with an increase in temperature. The V_{φ}^{0} values decrease in the following order: AQDPMS < MQDPMS < 3PQDPMS < 2PQDPMS. This result indicates that from 2PQDPMS to 3PQDPMS to MQDPMS to AQDPMS, the strengths of (solute-solvent) interactions increase leading to an increase in the 'electrostriction' effect, and resulting, therefore, in the contraction of the volume and hence the enhancement of the 'elasticity' of the solution [167-171]. The lower V_{φ}^{0} value for AQDPMS can be explained in terms of the more prominent 'electrostriction' effect which occurs in this system [172]. In addition to the

'electrostriction' effect, the size of the quinoxaline derivatives and consequently the degree of steric hindrance of the molecule are additional factors which affect the V_{φ}^{0} values [173].

The S_{v} values are positive for all systems at each temperature. The S_{v} value increases with an increase in temperature for all systems. The (solute-solute) interactions are stronger for MQDPMS than for AQDPMS than for 3PQDPMS than for 2PQDPMS. The (solute-solute) interaction increases with an increase in temperature for all systems. The B_{v} values are negative for all systems at each temperature. The B_{v} value decreases with an increase in temperature for all systems. The negative B_{v} values indicate an increase in (solute-solute) interactions for all systems and the simultaneous release of MQDPMS or AQDPMS or 2PQDPMS or 3PQDPMS to the bulk solvent [164].

The positive k_{φ}^{0} values of all systems may be interpreted in terms of an increase in the compressibility of the solution compared to the pure solvent MQDPMS or AQDPMS or 2PQDPMS or 3PQDPMS. This also indicates the presence of week solute-solvent interactions. Positive limiting apparent molar adiabatic compressibility, for MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS systems are due to the solvent intrinsic compressibility is greater than the penetration effect. These indicate that the MQDPMS or AQDPMS or 2PQDPMS or 3PQDPMS molecules being released from methyl acetate should present lesser resistance to compression than the bulk solvent. The k_{φ}^{0} value decreases with an increase in temperature. The S_{k} and B_{k} have the same meaning as S_{v} and B_{v}.

4.1.4. Thermal expansion coefficients (α_p)

The isobaric thermal expansion coefficient (α_p), of the solute was calculated using the apparent molar volume and apparent molar expansibility at infinite dilution data using the eqn (4.5)

$$\alpha_P = \frac{1}{V_\varphi^0}\left(\frac{\partial V_\varphi^0}{\partial T}\right)_P = \frac{E_\varphi^0}{V_\varphi^0} \qquad (4.5)$$

The isobaric thermal expansion coefficients, α_P, are given in **Table 4.1.4**

Table 4.1.4 The limiting apparent molar expansibility, E_φ^0 and isobaric thermal expansion coefficients α_P.

Solute	Solvent	$10^6 \times E_\varphi^0$ ($m^3 \cdot mol^{-1} \cdot K^{-1}$)			
		T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K
Methyl acetate	MQDPMS	-0.0360	-0.0359	-0.0358	-0.0357
Methyl acetate	AQDPMS	-0.0379	-0.0372	-0.0364	-0.0357
Methyl acetate	2PQDPMS	-0.0267	-0.0255	-0.0243	-0.0231
Methyl acetate	3PQDPMS	-0.0368	-0.0346	-0.0324	-0.0302
			$10^3 \times \alpha_P$ (K^{-1})		
Methyl acetate	MQDPMS	0.0189	0.0172	0.0158	0.0146
Methyl acetate	AQDPMS	0.0199	0.0177	0.0160	0.0145
Methyl acetate	2PQDPMS	0.0210	0.0182	0.0150	0.0140
Methyl acetate	3PQDPMS	0.0209	0.0179	0.0154	0.0134

It can be observed from the **Table 4.1.4** that the values of α_P show an overall decrease with increase in temperature. Further, the values of α_P of methyl acetate in aqueous solution of MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS have been compared, are show the order: MQDPMS < AQDPMS < 3PQDPMS < 2PQDPMS which is possibly due to the effect of the position of propanyl group as well as the replacement of propanyl group by methylsulphonyl and acetyl group on quinoxaline derivatives.

4.1.5. Limiting apparent molar expansivities

The temperature dependence of V_φ^0 can be expressed as [172]:

$$V_\varphi^0 = A + BT + CT^2 \tag{4.6}$$

where A, B and C are empirical parameters and T is the temperature. The limiting apparent molar expansibility E_φ^0 was obtained by differentiating Eq. (4.6) with respect to temperature.

$$E_\varphi^0 = \left(\frac{\partial V_\varphi^0}{\partial T}\right)_P = B + 2CT \tag{4.7}$$

The E_φ^0 values for each binary system are also presented in **Table 4.1.4** and provide important information about the (solute-solvent) interactions [174]. **Table 4.1.4** shows that at each temperature, E_φ^0 values are negative for all systems and increase with an increase in temperature. The increase in the E_φ^0 values with temperature indicate the increase in thermal agitation, resulting in MQDPMS, AQDPMS, 2PQDPMS or 3PQDPMS molecules being released from methyl acetate, thereby increasing the solution volume to a greater extent than for the pure solvent [175]. The negative values of E_φ^0 indicate the presence of week (solute-solvent) interactions in all the solutions investigated.

According to the Hepler's equation [176], the E_φ^0 is a linear function of temperature:

$$T\left(\frac{\partial^2 V_\varphi^0}{\partial T^2}\right)_P = -\left(\frac{\partial C_P}{\partial P}\right)_T \tag{4.8}$$

The signs of $\left(\partial^2 V_\varphi^0 / \partial T^2\right)_P$ values are a better criterion for characterising the long range structure making and breaking ability of the solute in the solution namely: (i) if $\left(\partial^2 V_\varphi^0 / \partial T^2\right)_P$

value is positive it means the solute is structure maker and (ii) if it is negative, the solute is a structure breaker. The values of $\left(\partial^2 V_\varphi^0 / \partial T^2\right)_P$ are 2.8×10^{-6}, 1.5×10^{-4}, 2.4×10^{-4} and 4.4×10^{-4} for methyl acetate in aqueous solution of MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS, respectively. Thus, the solute (methyl acetate) acts as a structure maker in the solutions [168]. The evidence for the relation between Hepler's constant and microscopic structure are shown in the literature [168].

4.1.6 Partial molar quantities of transfer

The partial molar volumes of transfer ΔV_φ^0 and partial molar adiabatic compressibility of transfer Δk_φ^0 from water to aqueous solutions of quinoxaline derivatives were calculated from following equation (4.9);

$$\Delta Y_\Phi^0 = Y_\Phi^0(in\ aqueous\ co-solute\ solution) - Y_\Phi^0(in\ waterorethanol) \qquad (4.9)$$

where Y_Φ^0 denotes to V_φ^0 and k_φ^0 and their corresponding values have been reported in **Table 4.1.5.** The system (methyl acetate + water) measured by Pal *et. al.*, [166] was used to calculate the partial molar volumes of transfer, ΔV_φ^0 and partial molar adiabatic compressibility of transfer, Δk_φ^0 from water to aqueous solutions of quinoxaline derivatives at studied temperature. A perusal of **Table 4.1.5** reveals that the values of ΔY_φ^0 are free from (solute-solute) interactions and therefore furnish information about (solute-solvent) interactions [176]. The values of ΔV_φ^0 are negative and decrease with an increase in temperature for all systems except for MQDPMS at T= 298.15 K. The negative value of ΔV_φ^0 of methyl acetate in aqueous solution of MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS may be attributed to the decrease in the solute-solvent interactions at infinite dilution [178].

Table 4.1.5 Partial molar volume of transfer (ΔV_{φ}^{0}), and partial molar adiabatic compressibility of transfer (Δk_{φ}^{0}) of methyl acetate (solute) in aqueous solution of MQDPMS or AQDPMS or 2PQDPMS or 3PQDPMS (solvent) at (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 Mpa.

T/K	10^6 X ΔV_{φ}^{0} /($m^3 \cdot mol^{-1}$)	10^6 X Δk_{φ}^{0} /($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)
Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} MQDPMS		
293.15	-2.00	13058.8
298.15	-2.18	12853.1
303.15	-2.37	12686.5
308.15	-2.55	12553.9
Methyl acetate + aqueous solution of 0.0006 mol·kg^{-1} AQDPMS		
293.15	-2.00	13106.1
298.15	-2.18	12897.7
303.15	-2.37	12727.8
308.15	-2.56	12594.3
Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 2PQDPMS		
293.15	-1.37	13579.3
298.15	-1.49	13362.3
303.15	-1.63	13185.5
308.15	-1.75	13050.0
Methyl acetate + aqueous solution of 0.0005 mol·kg^{-1} 3PQDPMS		
293.15	-1.85	12138.4
298.15	-2.03	11945.8
303.15	-2.20	11789.1
308.15	-2.36	11666.6

The values of Δk_{φ}^{0} are positive and decrease with an increase in temperature for all the systems. The values of Δk_{φ}^{0} decreases with temperature and this may be ascribed to increase of electrostricted water molecules around the MQDPMS, AQDPMS, 2PQDPMS and 3PQDPMS [179]. The Δk_{φ}^{0} values increase in the following order: 3PQDPMS < MQDPMS < AQDPMS < 2PQDPMS and is possibly due to the effect of position of propanyl group as well as replacement of propanyl group by methylsulphonyl and acetyl group on quinoxaline

derivatives. These results indicate that there is more solute-solvent interaction for 2PQDPMS solution as compared to AQDPMS, MQDPMS and 3PQDPMS due to the effect of position of propanyl group as well as replacement of propanyl group by methylsulphonyl and acetyl group on quinoxaline derivatives.

4.2 GROUP II: BQDB, 3MQDP, 3PQDB and 4CQDPP

4.2.1 Density and sound velocity measurement

The density (ρ), sound velocity (u), for the mixture of methyl acetate in alcoholic solution of quinoxaline derivatives BQDB, 3MQDP, 3PQDB and 4CQDPP were measured at 293.15, 298.15, 303.15 and 308.15 K and at pressure p = 0.1 MPa and the values are presented in **Table 4.2.1**

4.2.2. Apparent molar quantities

The apparent molar volume, V_φ, and apparent molar adiabatic compressibility, k_φ, are very useful parameters which give more information for investigating solute-solute and solute-solvent and solvent-solvent interactions. The apparent molar volume, V_φ, are explained as the limiting volume when a substance occupy in 1 mole of the other substance. In this limiting volume, the solute molecules are enclosed only by solvent molecules [180].

The apparent molar volume, V_φ, and apparent molar adiabatic compressibility, k_φ, were calculated using the experimental values of density and sound velocity by using the eqns. (4.1) and (4.2) which are given in group I set of quinoxaline derivatives

The experimental values of apparent molar volume, V_φ, and apparent molar adiabatic compressibility, k_φ, for the mixture of methyl acetate in alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP at T= 293.15, 298.15, 303.15 and 308.15 K and at pressure p = 0.1 MPa are also presented in **Table 4.2.1.**

Table 4.2.1 The density (ρ), sound velocity (u), apparent molar volume (V_φ), and apparent molar adiabatic compressibility (k_φ) for the mixture of methyl acetate in alcoholic solution of quinoxaline derivative BQDB, 3MQDP, 3PQDB and 4CQDPP at 293.15, 298.15, 303.15 and 308.15 K and at pressure p = 0.1 MPa.

m (mol·kg^{-1})	ρ (kg·m^{-3})	u (m·s^{-1})	V_φ (m^3·mol^{-1})	k_φ (m^3·mol^{-1}·Pa^{-1})
Methyl acetate + alcoholic solution of 0.0005 mol·kg^{-1} BQDB				
		T = 293.15 K		
0.0570	794.66	1168.7	0.0034	5.8987
0.1044	794.96	1168.0	0.0019	3.2667
0.1151	795.10	1167.9	0.0017	2.9697
0.3388	796.54	1166.8	0.0006	1.0592
0.5637	797.82	1165.0	0.0004	0.6705
0.7910	799.27	1165.2	0.0003	0.4964
1.0130	800.66	1164.0	0.0003	0.4046
1.2390	802.07	1164.8	0.0002	0.3414
1.4657	803.55	1165.0	0.0002	0.2982
1.6888	804.75	1166.0	0.0002	0.2664
		T = 298.15 K		
0.0570	790.44	1151.0	0.0034	5.9450
0.1044	790.68	1150.5	0.0019	3.2917
0.1151	790.81	1150.0	0.0017	3.0003
0.3388	792.06	1147.0	0.0006	1.0856
0.5637	793.42	1146.2	0.0004	0.6837
0.7910	794.85	1144.9	0.0003	0.5109
1.0130	796.11	1144.0	0.0003	0.4164
1.2390	797.79	1144.8	0.0002	0.3508
1.4657	798.99	1145.0	0.0002	0.3073
1.6888	800.27	1147.0	0.0002	0.2731
		T = 303.15 K		
0.0570	786.13	1133.2	0.0033	5.9935
0.1044	786.45	1132.2	0.0019	3.3285
0.1151	786.52	1132.8	0.0017	3.0146
0.3388	787.76	1130.9	0.0006	1.0862
0.5637	789.02	1129.0	0.0004	0.6904
0.7910	790.37	1128.0	0.0003	0.5161
1.0130	791.69	1129.1	0.0003	0.4164
1.2390	793.25	1128.8	0.0002	0.3536
1.4657	794.50	1129.0	0.0002	0.3099
1.6888	795.74	1130.0	0.0002	0.2771
		T = 308.15 K		
0.0570	781.80	1120.0	0.0033	5.7944
0.1044	782.09	1119.4	0.0019	3.2138
0.1151	782.23	1119.1	0.0017	2.9265
0.3388	783.71	1116.8	0.0006	1.0590
0.5637	785.25	1115.2	0.0004	0.6725

0.7910	786.73	1114.0	0.0003	0.5042
1.0130	788.06	1113.3	0.0003	0.4119
1.2390	789.36	1112.8	0.0002	0.3516
1.4657	790.68	1113.0	0.0002	0.3084
1.6888	791.87	1115.1	0.0002	0.2745

Methyl acetate + alcoholic solution of 0.0005 mol·kg^{-1} 3MQDP

T = 293.15 K

0.1040	793.80	1164.2	0.0019	3.3841
0.1162	793.88	1163.7	0.0017	3.0460
0.3395	795.86	1160.0	0.0006	1.1043
0.5636	797.83	1161.2	0.0004	0.6846
0.7887	799.60	1163.1	0.0003	0.5018
1.0154	801.14	1166.0	0.0003	0.3982
1.2406	802.81	1169.2	0.0002	0.3316
1.4676	804.13	1171.0	0.0002	0.2879

T = 298.15 K

0.1040	789.35	1150.0	0.0019	3.3524
0.1162	789.53	1149.0	0.0017	3.0248
0.3395	791.54	1146.0	0.0006	1.0948
0.5636	793.45	1147.0	0.0004	0.6805
0.7887	795.11	1149.5	0.0003	0.4981
1.0154	796.70	1151.9	0.0003	0.3964
1.2406	798.39	1153.6	0.0002	0.3329
1.4676	799.66	1154.0	0.0002	0.2915

T = 303.15 K

0.1040	785.08	1131.1	0.0019	3.4061
0.1162	785.23	1130.8	0.0017	3.0614
0.3395	787.16	1129.4	0.0006	1.1001
0.5636	789.17	1129.5	0.0004	0.6876
0.7887	790.92	1130.8	0.0003	0.5066
1.0154	792.47	1133.0	0.0003	0.4039
1.2406	793.96	1135.0	0.0002	0.3393
1.4676	795.13	1136.5	0.0002	0.2958

T = 308.15 K

0.1040	780.60	1113.1	0.0019	3.4167
0.1162	780.75	1112.7	0.0017	3.0736
0.3395	782.69	1112.4	0.0006	1.0987
0.5636	784.55	1112.0	0.0004	0.6908
0.7887	786.15	1113.0	0.0003	0.5111
1.0154	787.67	1114.1	0.0003	0.4106
1.2406	789.17	1115.0	0.0002	0.3473
1.4676	790.57	1118.2	0.0002	0.2994

Methyl acetate + alcoholic solution of 0.0003 mol·kg^{-1} 3PQDB

T = 293.15 K

0.0562	793.44	1167.5	0.0035	6.0872
0.1041	793.88	1166.9	0.0019	3.3253
0.1141	793.93	1166.0	0.0017	3.0560
0.4359	796.46	1164.6	0.0005	0.8531
0.5643	797.36	1166.5	0.0004	0.6669

0.7882	798.90	1167.1	0.0003	0.4942
1.0124	800.53	1165.6	0.0003	0.4018
1.2401	801.92	1164.2	0.0002	0.3426
1.4632	803.13	1163.0	0.0002	0.3025
1.6891	804.38	1161.0	0.0002	0.2736
		T = 298.15 K		
0.0562	789.16	1151.1	0.0034	6.0940
0.1041	789.59	1150.5	0.0019	3.3310
0.1141	789.65	1150.1	0.0017	3.0527
0.4359	791.97	1149.1	0.0005	0.8538
0.5643	792.85	1148.0	0.0004	0.6793
0.7882	794.49	1147.5	0.0003	0.5065
1.0124	796.11	1148.0	0.0003	0.4078
1.2401	797.46	1147.4	0.0002	0.3467
1.4632	798.71	1146.7	0.0002	0.3056
1.6891	799.91	1146.0	0.0002	0.2751
		T = 303.15 K		
0.0562	784.83	1130.4	0.0034	6.2634
0.1041	785.25	1132.0	0.0019	3.3771
0.1141	785.35	1133.0	0.0017	3.0668
0.4359	787.58	1132.2	0.0005	0.8595
0.5643	788.59	1131.2	0.0004	0.6833
0.7882	790.03	1130.0	0.0003	0.5131
1.0124	791.53	1129.2	0.0003	0.4169
1.2401	792.83	1128.4	0.0002	0.3553
1.4632	794.05	1127.0	0.0002	0.3147
1.6891	795.19	1128.0	0.0002	0.2811
		T = 308.15 K		
0.0562	780.46	1116.3	0.0034	6.1101
0.1041	780.78	1116.0	0.0019	3.3402
0.1141	780.88	1115.0	0.0017	3.0739
0.4359	783.16	1114.0	0.0005	0.8644
0.5643	784.00	1113.4	0.0004	0.6874
0.7882	785.51	1113.7	0.0003	0.5120
1.0124	786.97	1114.0	0.0003	0.4142
1.2401	788.39	1112.5	0.0002	0.3548
1.4632	789.73	1111.2	0.0002	0.3143
1.6891	791.01	1110.7	0.0002	0.2831
	Methyl acetate + alcoholic solution of 0.0011 mol·kg^{-1} 4CQDPP			
		T = 293.15 K		
0.0597	794.36	1172.4	0.0032	5.5285
0.1013	794.45	1171.7	0.0019	3.3046
0.1215	794.54	1171.0	0.0016	2.7800
0.3401	796.01	1170.0	0.0006	1.0408
0.5644	797.48	1169.3	0.0004	0.6559
0.7893	799.28	1168.8	0.0003	0.4877
1.0155	801.04	1167.6	0.0003	0.3951
1.2383	802.56	1166.8	0.0002	0.3368
1.4636	803.67	1165.9	0.0002	0.2969
1.6906	804.62	1164.0	0.0002	0.2691

		***T* = 298.15 K**		
0.0597	790.08	1155.0	0.0032	5.5591
0.1013	790.28	1154.5	0.0019	3.3173
0.1215	790.34	1154.0	0.0016	2.7889
0.3401	791.58	1153.0	0.0006	1.0481
0.5644	793.13	1151.1	0.0004	0.6657
0.7893	795.10	1150.2	0.0003	0.4959
1.0155	796.73	1149.5	0.0003	0.4015
1.2383	797.72	1148.9	0.0002	0.3436
1.4635	799.22	1148.4	0.0002	0.3017
1.6906	800.14	1147.0	0.0002	0.2731
		***T* = 303.15 K**		
0.0597	785.75	1139.0	0.0032	5.5327
0.1013	785.83	1138.7	0.0019	3.3029
0.1215	785.90	1138.8	0.0016	2.7667
0.3401	787.52	1137.0	0.0006	1.0438
0.5644	788.73	1136.7	0.0004	0.6600
0.7893	790.66	1135.6	0.0003	0.4933
1.0155	792.23	1134.0	0.0003	0.4024
1.2383	793.24	1133.0	0.0002	0.3456
1.4636	794.72	1132.6	0.0002	0.3037
1.6906	795.61	1131.4	0.0002	0.2751
		***T* = 308.15 K**		
0.0597	781.48	1119.0	0.0032	5.5949
0.1013	781.67	1118.6	0.0019	3.3403
0.1215	781.64	1118.0	0.0016	2.8148
0.3401	783.11	1117.7	0.0006	1.0548
0.5644	784.29	1116.0	0.0004	0.6743
0.7893	786.19	1115.3	0.0003	0.5034
1.0155	787.77	1114.8	0.0003	0.4084
1.2383	788.71	1114.0	0.0002	0.3512
1.4636	790.18	1113.5	0.0002	0.3091
1.6906	791.04	1112.3	0.0002	0.2804

The experimental values given in **Table 4.2.1** of density(ρ) and sound velocity (u) for methyl acetate in 0.0005, 0.0005, 0.0003, 0.0011 mol.kg^{-1} alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP, respectively against the molality of methyl acetate at different temperatures have been plotted in **Figs. 4.2.1(a-d) and 4.2.2(a-d).**

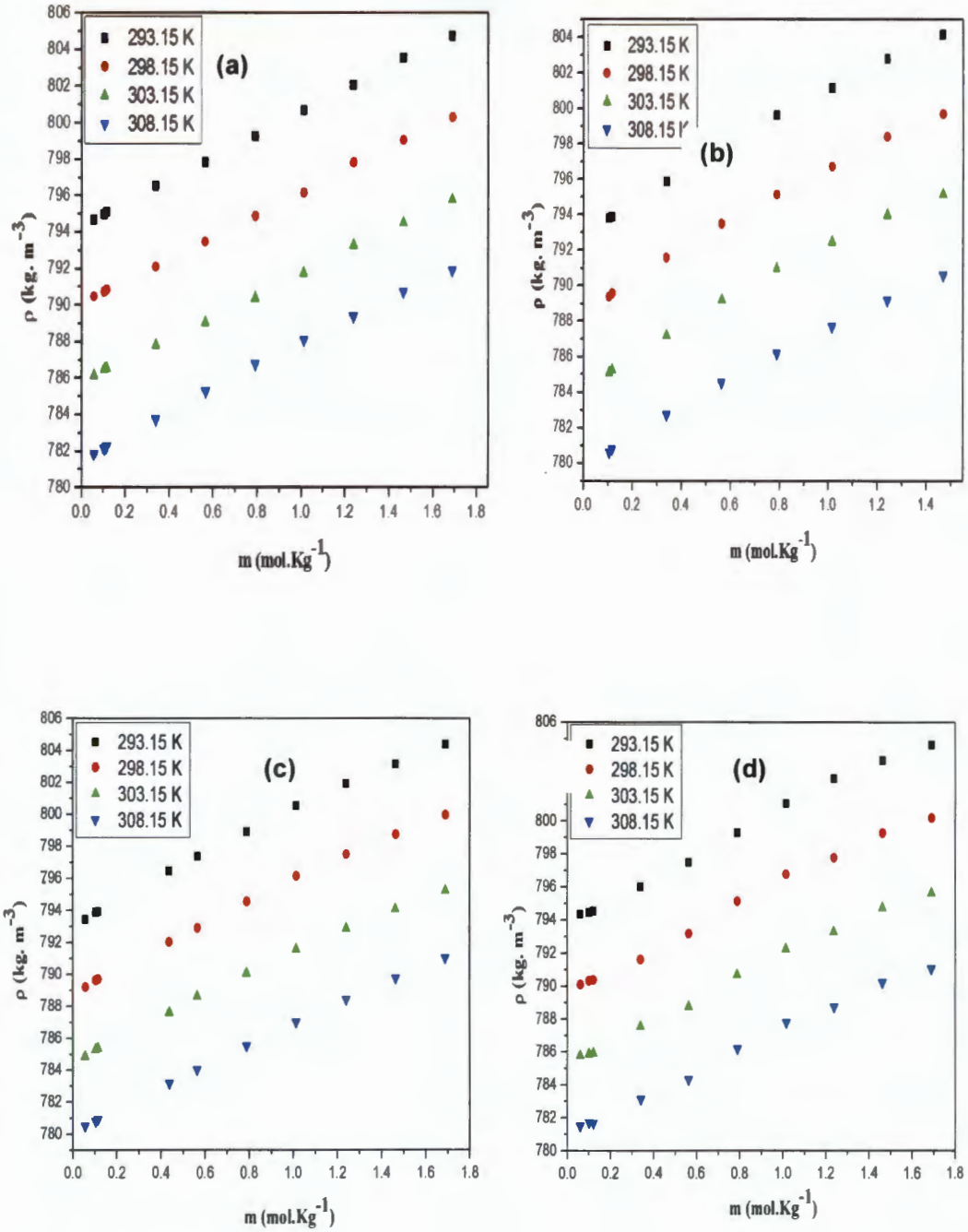


Fig. 4.2.1. Density, ρ, for the mixture of methyl acetate in alcoholic solution of (a) BQDB, (b) 3MQDP, (c) 3PQDB, (d) 4CQDPP at 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

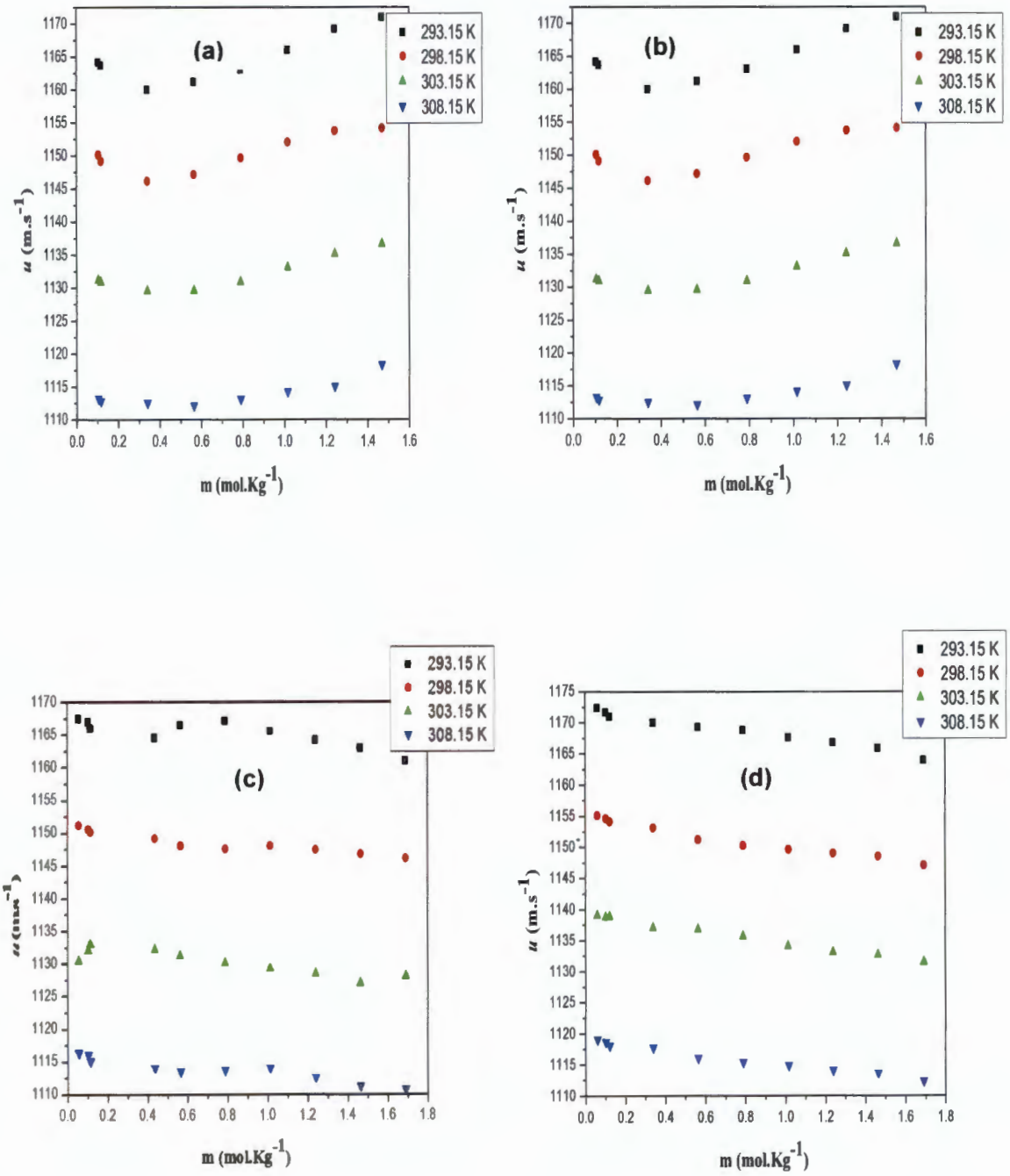


Fig. 4.2.2. Sound velocity, *u*, for the mixture of methyl acetate in alcoholic solution of (a) BQDB, (b) 3MQDP, (c) 3PQDB, (d) 4CQDPP at 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

From the Figs. 4.2.1 (a-d) and 4.2.2 (a-d), it can be observed that the density values increased with an increase in concentration and decreased with increase in temperature while sound velocity values exhibits the decreasing temperature. The increasing values of density suggest the presence of strong intermolecular attraction such as solute-solvent attraction [163]. An increase in concentration makes the solute and solvent molecules get closer approach and results in strong association between solute and solvent molecules. This leads to decrease in the volume and an increase in the density of the solution.

It is also observed that based on the structure and property of solute, the sound velocity values increase or decrease [163]. If the solute increases the sound velocity values, then it is a structure maker and if it decreases then it is structure breaker. The decrease in sound velocity indicates that the interaction between solute and solvent is becoming less dominant. This is due to the replacement of strong intermolecular attraction between solvent molecules by weaker intermolecular interactions. This indicates that the solvent-solvent interaction is replaced by solute-solvent interaction.Thus, methyl acetate (solute) which is used in group II compounds decreases the values of sound velocity and therefore it acts as a structure breaker.

The values given in **Table 4.2.1** of V_φ and k_φ for methyl acetate in 0.0005, 0.0005, 0.0003, 0.0011 $mol.kg^{-1}$ alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP, respectively against the molality of methyl acetate at different temperatures have been plotted in **Figs. 4.2.3 (a-d) and 4.2.4 (a-d).**

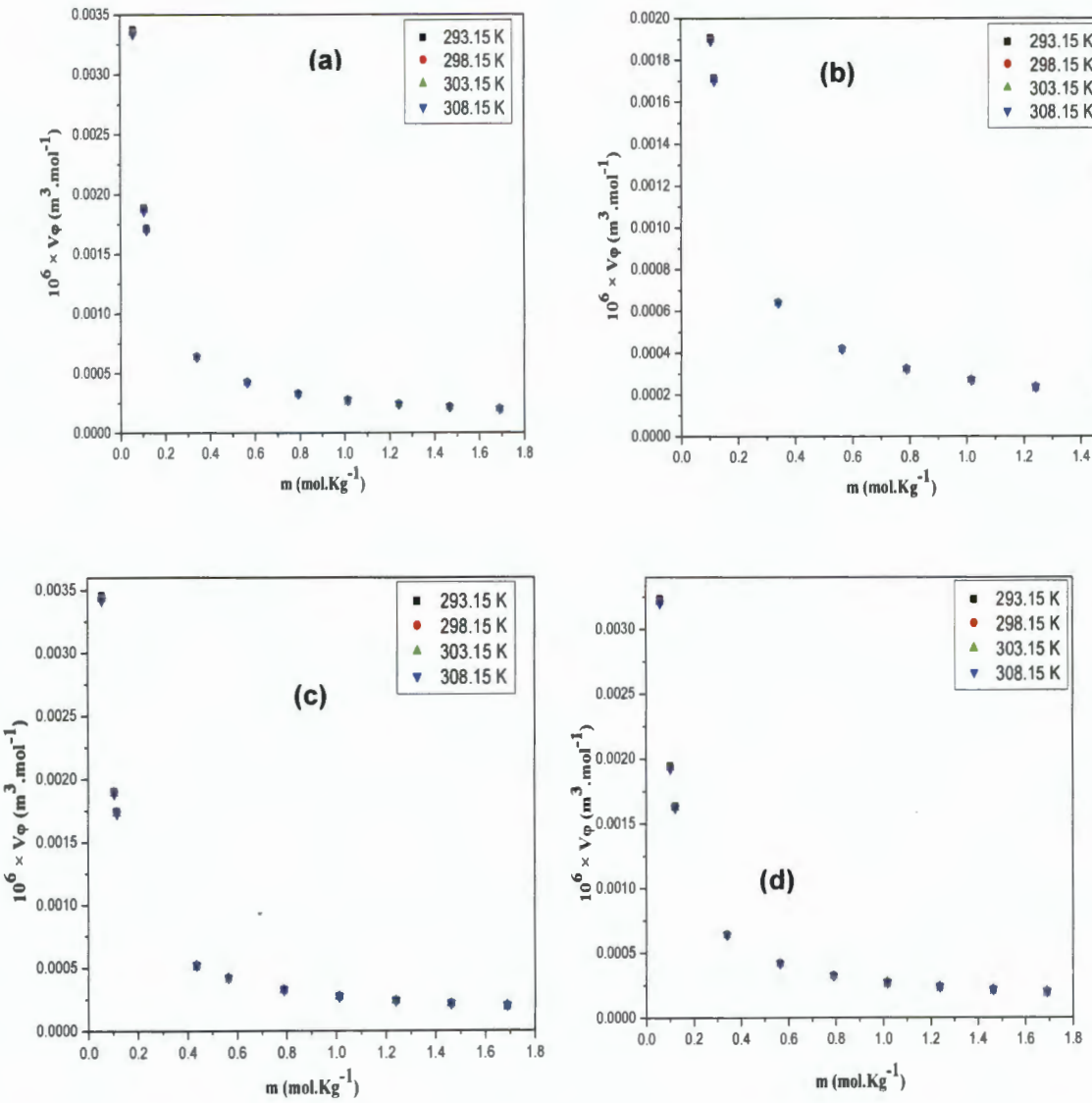


Fig. 4.2.3. Apparent molar volume, $V\varphi$, for the mixture of methyl acetate in alcoholic solution of (a) BQDB, (b) 3MQDP, (c) 3PQDB, (d) 4CQDPP at 293.15 K (■), T= 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

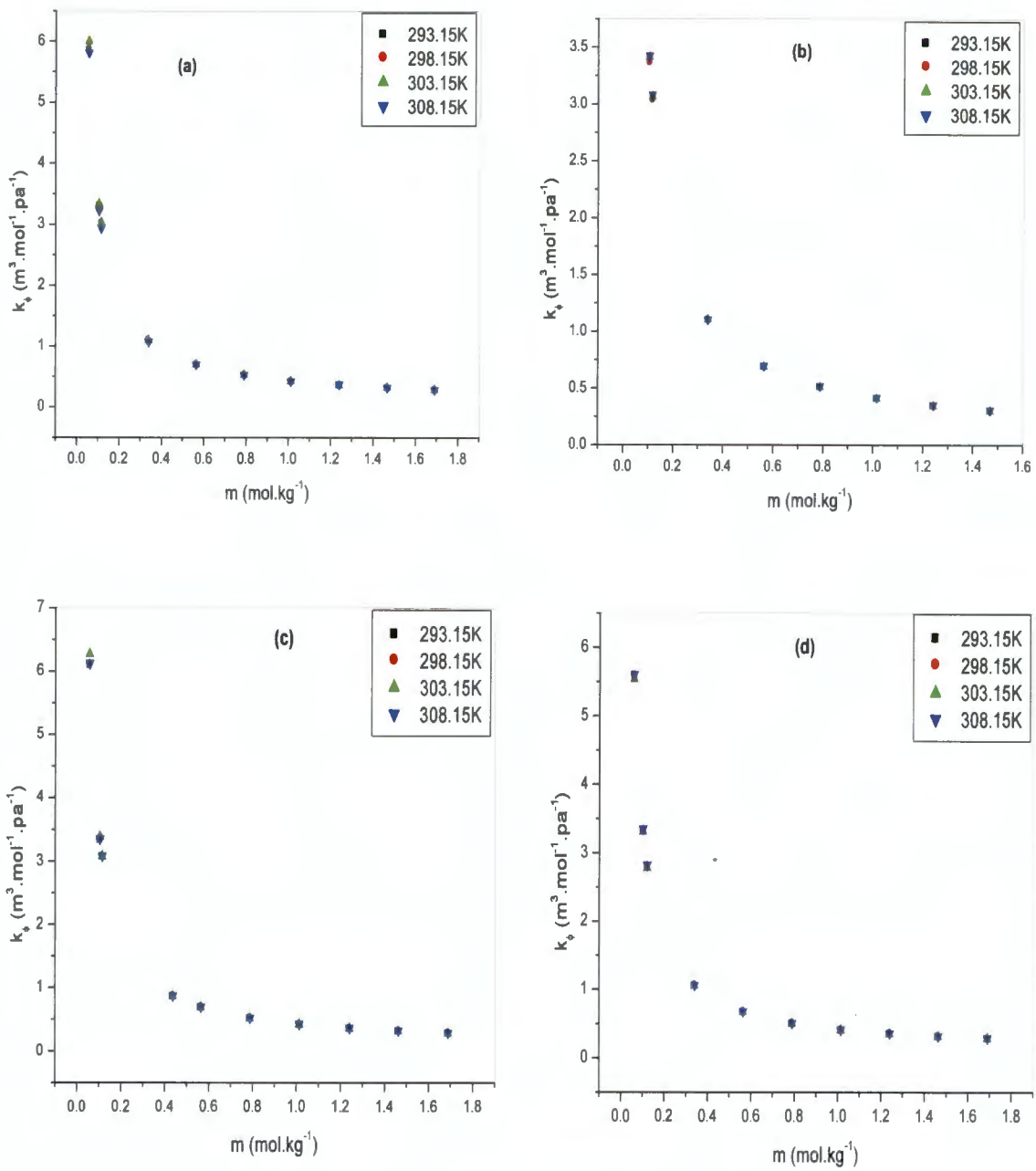


Fig. 4.2.4. Apparent molar adiabatic compressibility, $k\varphi$, for the mixture of methyl acetate in alcoholic solution of (a) [BQDB], (b) [3MQDP], (c) [3PQDB], (d) [4CQDPP] at T= 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

The apparent molar properties reflect more appropriately the interactions and structural changes induced by added quantities of a second compound [181]. From the **Fig. 4.2.3 (a-d),** it can be observed that the apparent molar volume V_φ decreases with increase in concentration of solute for each binary system which is opposite to group I set of compounds. The positive V_φ values are small and unaffected with an increase in temperature and follow similar trend in each system. It is also noted that the V_φ values are high at low concentration. The V_φ values are positive which suggests that the overall structural order is enhanced in solution.

Fig. 4.2.4 (a-d), shows that the apparent molar adiabatic compressibility, k_φ, values decreases with an increase in concentration of solute at a fixed temperature for all the systems. It is also observed that k_φ, values are positive for all the systems which indicate that methyl acetate rich region is more compressible as compared with bulk solution [166]. The positive k_φ, values are attributed to the weak attractive interactions between solute and solvent molecules. Further, the values of k_φ of methyl acetate in alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP have been compared, and show the order: BQDB = 4CQDPP and 3PQDB > 3MQDP.

4.2.3 Apparent molar quantities at infinite dilution

The variation of apparent molar volume, V_φ, and apparent molar adiabatic compressibility, k_φ, with the concentration can be represented by the Redlich-Mayer type [182] using eqs 4.3 and 4.4. The limiting apparent molar volume, V_φ^0, is the limiting volume that a substance occupies in one mole of other substance [180]. The values of limiting apparent molar volume V_φ^0 and apparent molar adiabatic compressibility, k_φ^0 and slopes S_v, B_v, S_k and B_k and standard errors (obtained by least squares fitting of V_φ^0 and k_φ^0 values to eqns. (4.3) and (4.4)) have been presented in **Table 4.2.2 and 4.2.3**

Table 4.2.2 Limiting apparent molar volumes, V_{φ}^{0}, and fitting parameters S_V and B_V of methyl acetate (solute) in alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP and at (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 MPa.

T (K)	V_{φ}^{0} ($m^3.mol^{-1}$)	S_V ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$)	B_V ($m^3 \cdot mol^{-2} \cdot kg$)	σ
Methyl acetate + alcoholic solution of 0.0005 mol.kg^{-1} BQDB				
293.15	0.005	-0.009	0.005	0.0004
298.15	0.005	-0.009	0.005	0.0004
303.15	0.005	-0.009	0.004	0.0003
308.15	0.005	-0.009	0.004	0.0003
Methyl acetate + alcoholic solution of 0.0005 mol·kg^{-1} 3MQDP				
293.15	0.004	-0.007	0.003	0.0001
298.15	0.004	-0.007	0.003	0.0001
303.15	0.004	-0.007	0.003	0.0001
308.15	0.004	-0.007	0.003	0.0001
Methyl acetate + alcoholic solution of 0.0003mol·kg^{-1} 3PQDB				
293.15	0.005	-0.009	0.004	0.0004
298.15	0.005	-0.009	0.004	0.0003
303.15	0.005	-0.009	0.004	0.0003
308.15	0.005	-0.009	0.004	0.0003
Methyl acetate + alcoholic solution of 0.0011 mol·kg^{-1} 4CQDPP				
293.15	0.004	-0.009	0.004	0.0003
298.15	0.004	-0.009	0.004	0.0003
303.15	0.004	-0.009	0.004	0.0003
308.15	0.004	-0.009	0.004	0.0003

For the binary systems at infinite dilution, each ion is surrounded by methyl acetate (solute) and is at infinitely large distance from the other ions. Therefore, the V_φ^0 values in **Table 4.2.2** are unaffected by ion-ion interaction and measures only ion- solvent interaction. **Table 4.2.2** shows that V_φ^0 values are positive for all the systems and no effect of temperatute. This indicates the presence of strong solute–solvent interactions. The lower values of V_φ^0 for all systems can be explained in terms of the more prominent 'electrostriction' effect which occurs in the system. In addition, to the 'electrostriction' effect, the size of the quinoxaline derivatives and consequently the degree of steric hindrance of the molecule are additional factors which affect the V_φ^0 values. The S_V values are negative for all systems at each temperature. The S_V values for systems BQDB, 3PQDB, 4CQDPP are same and lower than 3MQDP system suggest that (solute-solute) interactions are stronger for 3MQDP than for others BQDB, 3PQDB, 4CQDPP. The Bv values are positive for all systems. The Bv values of 3MQDP system are smaller than the other three systems.

Table 4.2.3 Limiting apparent molar adiabatic compressibility, k_{φ}^{0}, and fitting parameters S_k and B_k, of methyl acetate (solute) in alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP at (293.15, 298.15, 303.15 and 308.15) K and at pressure $p = 0.1$ MPa.

T (K)	k_{φ}^{0} ($m^3.mol^{-1}.pa^{-1}$)	S_k ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2} pa^{-1}$)	B_k ($m^3 \cdot mol^{-2} \cdot kg.\ pa^{-1}$)	σ
Methyl acetate + alcoholic solution of 0.0005 mol.kg^{-1} BQDB				
293.15	8.1	-15.9	7.7	0.6
298.15	8.2	-16.0	7.8	0.6
303.15	8.3	-16.1	7.9	0.6
308.15	8.4	-16.2	8.0	0.6
Methyl acetate + alcoholic solution of 0.0005 mol·kg^{-1} 3MQDP				
293.15	6.6	-12.3	6.1	0.2
298.15	6.7	-12.4	6.2	0.2
303.15	6.8	-12.5	6.3	0.2
308.15	6.9	-12.6	6.4	0.2
Methyl acetate + alcoholic solution of 0.0003 mol·kg^{-1} 3PQDB				
293.15	8.3	-16.1	7.8	0.6
298.15	8.4	-16.2	7.9	0.6
303.15	8.5	-16.3	8.1	0.7
308.15	8.6	-16.4	8.2	0.6
Methyl acetate + alcoholic solution of 0.0011 mol·kg^{-1} 4CQDPP				
293.15	7.6	-15.1	7.3	0.6
298.15	7.7	-15.2	7.4	0.6
303.15	7.8	-15.3	7.5	0.6
308.15	7.9	-15.4	7.6	0.6

The k_{φ}^{0} values are positive and increased with increase in temperature for all systems. The solutes which bring less electrostriction lead to an increase in the compressibility of solution as compared to the solvent BQDB, 3MQDP, 3PQDB and 4CQDPP which is revealed by the positive values of limiting apparent molar adiabatic compressibility in all the binary systems shown in **Table 4.2.3.** Hydrophilic solutes often show positive compressibilities as a result of the order they prompt in the water structure [183].

The compressibility of H-bonded structures differs based on the kind of the H-bonds present. The positive limiting apparent molar adiabatic compressibility, for BQDB, 3MQDP, 3PQDB and 4CQDPP systems are caused by the solvent intrinsic compressibility which are larger than the penetration effect. This shows that the BQDB, 3MQDP, 3PQDB and 4CQDPP molecules being released from methyl acetate should have lesser resistance to compression than the bulk solvent. The parameters S_{k} and B_{k} have the same meaning as S_{v} and B_{v}.

4.2.4. Thermal expansion coefficients (α_p)

The isobaric thermal expansion coefficient, α_p, of the solute can be calculated using apparent molar volume and apparent molar expansivity at infinite dilution data using the eqn.(4.5), and the values of (α_p) are presented in **Table 4.2.4.**

Table 4.2.4 The limiting apparent molar expansibility, E_{φ}^{0} and isobaric thermal expansion coefficients α_p.

Solute	Solvent	E_{φ}^{0} ($m^3 \cdot mol^{-1} \cdot K^{-1}$)			
		$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K
Methyl acetate	BQDB	0.0457	0.0458	0.0459	0.0460
Methyl acetate	3MQDP	0.0457	0.0464	0.0472	0.0479
Methyl acetate	3PQDB	0.0231	0.0343	0.0355	0.0367
Methyl acetate	4CQDPP	0.0302	0.0324	0.0346	0.0368
			α_p (K^{-1})		
Methyl acetate	BQDB	0.0185	0.0168	0.0154	0.0142
Methyl acetate	3MQDP	0.0195	0.0173	0.0155	0.0140
Methyl acetate	3PQDB	0.0203	0.0175	0.0144	0.0132
Methyl acetate	4CQDPP	0.0200	0.0170	0.0150	0.0130

It can be observed from the **Table 4.2.4** that the values of α_P exhibits an overall decrease with increase in temperature.

4.2.5. Limiting apparent molar expansivities (E_{φ}^{0})

The temperature dependence of V_{φ}^{0} can be expressed by using eqn (4.6)

The limiting apparent molar expansibility (E_{φ}^{0}), can be obtained by differentiating the eqn (4.6) with respect to temperature.The limiting apparent molar expansibility values provide important information about solute-solvent interactions which takes place in the solution.

The values of E_{φ}^{0} for all the systems are also presented in **Table 4.2.4.** The E_{φ}^{0} values for all the systems are also presented in **Table 4.2.4** and provide important information about the (solute-solvent) interactions. **Table 4.2.4** shows that at each temperature E_{φ}^{0} values are positive for all the systems and increases with an increase in temperature. The increase in the E_{φ}^{0} values with temperature indicate increase in thermal agitation, resulting in BQDB, 3MQDP, 3PQDB and 4CQDPP molecules being released from methyl acetate, thereby

increasing the solution volume to a greater extent than for the solvent. The positive values of E_{φ}^{0} indicate the presence of strong solute-solvent interactions in all the solutions investigated. According to the Hepler's equation [176], the E_{φ}^{0} is a linear function of temperature. In recent years, it has been emphasized by different investigators that S_v is not the sole criterion for determining the structure making or breaking nature of any solute. Therefore, Hepler and Loren developed a technique to examine the sign of $\left(\partial^2 V_{\varphi}^{0} / \partial T^2\right)_P$ for solutes in terms of long range structure making or breaking capacities of the solutes using the general thermodynamic expression;

(i) if $\left(\partial^2 V_{\varphi}^{0} / \partial T^2\right)_P$ value is positive it means the solute is structure maker and (ii) if it is negative, the solute is a structure breaker. The evidence for the relation between Hepler's constant and microscopic structure are shown in the literature.

4.2.6 Partial molar quantities of transfer

The partial molar volumes of transfer ΔV_{φ}^{0} and partial molar adiabatic compressibility of transfer Δk_{φ}^{0} from ethanol to alcoholic solutions of quinoxaline derivatives were calculated from eqn (4.9) and the corresponding ΔV_{φ}^{0}, Δk_{φ}^{0} values have been reported in **Table 4.2.5.** The data reported in Table 1A, density (ρ), sound velocity (u), apparent molar volume (V_{φ}), and apparent molar adiabatic compressibility (k_{φ}) of ethanol + methyl acetate system 293.15, 298.15, 303.15 and 308.15 K and at pressure p = 0.1 MPa were used to calculate partial molar quantities of transfer for Group II and III.

Table 4.2.5 Partial molar volume of transfer, ΔV_{φ}^{0}, and partial molar adiabatic compressibility of transfer, Δk_{φ}^{0}, of methyl acetate (solute) in alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP at (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 MPa.

T (K)	ΔV_{φ}^{0} ($m^3 \cdot mol^{-1}$)	Δk_{φ}^{0} ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)
Methyl acetate + alcoholic solution of 0.0005 mol.kg-1 BQDB		
293.15	-0.020	-0.3
298.15	-0.026	-0.4
303.15	-0.028	-0.5
308.15	-0.030	-1.1
Methyl acetate + alcoholic solution of 0.0005 mol·kg^{-1} 3MQDP		
293.15	-0.021	-1.9
298.15	-0.024	-2.0
303.15	-0.027	-2.2
308.15	-0.029	-2.4
Methyl acetate + aqueous solution of 0.0003 mol·kg^{-1} 3PQDB		
293.15	-0.019	-0.2
298.15	-0.022	-0.3
303.15	-0.026	-0.5
308.15	-0.028	-0.7
Methyl acetate + alcoholic solution of 0.0011 mol·kg^{-1} 4CQDPP		
293.15	-0.018	-0.7
298.15	-0.022	-0.8
303.15	-0.028	-0.9
308.15	-0.032	-1.2

The system (ethanol + methyl acetate) were measured and used to calculate partial molar volume of transfer, ΔV_{φ}^{0}, and partial molar adiabatic compressibility of transfer, ΔK_{φ}^{0}, from ethanol to alcoholic solutions of quinoxaline derivatives at studied temperatures. The **Table 4.2.5** shows that the values of ΔY_{φ}^{0} are free from solute-solute interaction and therefore provide information about solute-solvent interactions. The values of ΔV_{φ}^{0} are negative and decreases with an increase in temperature for all the systems. The negative values of ΔV_{φ}^{0} of methyl acetate in alcoholic solution of BQDB, 3MQDP, 3PQDB and 4CQDPP may be attributed to the decreasing solute-solvent interactions at infinite dilution. The ΔK_{φ}^{0} values are negative and

decreases with increase in temperature for all the binary systems. This may be ascribed to increasing of elecrostricted water molcules around each system. The ΔK_{φ}^{0} values increase in the following order: 3MQDP < 4CQDPP < BQDB < 3PQDB. This results indicate that there is more solute-solvent interaction for 3PQDB solution as compared to BQDB, 4CQDPP and 3MQDP.

4.3 GROUP III: 2PQDE, 4MQDPB, 2EQDPB and 4MQDB

4.3.1 Density and sound velocity measurement

The density (ρ), sound velocity (u), for the mixture of methyl acetate in alcoholic solution of quinoxaline derivative 2PQDE, 4MQDPB, 2EQDPB and 4MQDB were measured at T= (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 MPa and the data are presented in **Table 4.3.1.**

4.3.2 Apparent molar quantities

The apparent molar volume, V_φ, and apparent molar adiabatic compressibility, k_φ, were calculated by using the experimental density and sound velocity values by using the equations (4.1) and (4.2) which are given in Group I. The resulting values of apparent molar volume, V_φ, and apparent molar adiabatic compressibility, k_φ, for the mixture of methyl acetate in alcoholic solution of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB at 293.15, 298.15, 303.15 and 308.15 K and at pressure p= 0.1 MPa are also presented in **Table 4.3.1**

Table 4.3.1 Densities (ρ), sound velocities (u), apparent molar volume (V_φ) apparent molar adiabatic compressibility (k_φ), and molality (m), of methyl acetate (solute) in (ethanol + 2PQDE, 4MQDPB, 2EQDPB and 4MQDB (solvent) at 293.15, 298.15, 303.15 and 308.15 K and at pressure p = 0.1Mpa.

m (mol.Kg^{-1})	ρ (kg m^{-3})	u (m.s^{-1})	V_φ (m^3.mol^{-1})	k_φ (m^3.mol^{-1}.Pa^{-1})
Methyl acetate + alcoholic solution of 0.0005 mol.kg^{-1} 2PQDE				
		T = 293.15 K		
0.0630	795.34	1168.8	0.0030	5.3
0.1036	796.49	1170.3	0.0019	3.2
0.1180	795.27	1170.8	0.0017	2.8
0.3426	797.66	1175.9	0.0006	1.0
0.5826	797.99	1181.4	0.0004	0.6
0.7941	801.24	1185.7	0.0003	0.4
1.0204	802.07	1190.1	0.0003	0.3
1.2431	802.36	1194.7	0.0002	0.3
1.4798	805.38	1198.1	0.0002	0.2
1.7050	805.71	1200.9	0.0002	0.2
		T = 298.15 K		
0.0630	791.06	1155.0	0.0032	5.2
0.1036	792.20	1155.4	0.0019	3.2
0.1180	790.98	1155.7	0.0017	2.8
0.3426	793.35	1159.9	0.0006	1.0
0.5826	793.65	1164.9	0.0004	0.6
0.7941	796.88	1169.5	0.0003	0.4
1.0204	797.66	1175.1	0.0003	0.3
1.2431	797.96	1179.9	0.0002	0.3
1.4798	801.06	1183.2	0.0002	0.2
1.7050	801.25	1187.5	0.0002	0.2
		T = 303.15 K		
0.0630	786.72	1145.1	0.0033	5.0
0.1036	787.86	1145.8	0.0020	3.0
0.1180	786.64	1146.5	0.0018	2.7
0.3426	788.98	1149.4	0.0007	0.9
0.5826	789.26	1154.4	0.0004	0.6
0.7941	792.46	1157.5	0.0003	0.4
1.0204	793.20	1161.5	0.0003	0.3
1.2431	793.51	1165.1	0.0002	0.3
1.4798	796.69	1169.1	0.0002	0.2
1.7050	796.74	1172.1	0.0002	0.2
		T = 308.15 K		
0.0630	782.35	1136.2	0.0034	4.6
0.1036	783.48	1136.8	0.0021	2.8
0.1180	782.26	1137.2	0.0019	2.5

0.3426	784.57	1140.1	0.0007	0.9
0.5826	784.84	1143.2	0.0004	0.5
0.7941	788.00	1146.1	0.0003	0.4
1.0204	788.70	1149	0.0003	0.3
1.2431	789.02	1152.5	0.0003	0.3
1.4798	792.27	1155.4	0.0002	0.2
1.7050	792.19	1158.1	0.0002	0.2

Methyl acetate + alcoholic solution of 0.0003 mol.kg^{-1} 4MQDPB

T = 293.15 K

0.0592	795.80	1175.8	0.0032	5.4
0.1025	795.67	1176.1	0.0019	3.1
0.1192	796.48	1176.2	0.0016	2.7
0.3412	793.82	1177	0.0006	1.0
0.5671	799.45	1177.8	0.0004	0.6
0.7874	798.87	1178.5	0.0003	0.5
1.0140	801.04	1179.3	0.0003	0.4
1.2380	801.69	1180.2	0.0002	0.3
1.4665	802.37	1181.3	0.0002	0.3
1.6901	804.13	1182.1	0.0002	0.2

T = 298.15 K

0.0592	791.51	1157.6	0.0033	5.4
0.1025	791.37	1157.9	0.0020	3.2
0.1192	792.19	1158.2	0.0017	2.7
0.3412	789.51	1159.8	0.0007	1.0
0.5671	795.09	1161.1	0.0004	0.6
0.7874	794.52	1162.8	0.0003	0.5
1.0140	796.66	1164.4	0.0003	0.4
1.2380	797.30	1165.9	0.0002	0.3
1.4665	797.96	1167.5	0.0002	0.3
1.6901	799.69	1169.5	0.0002	0.2

T = 303.15 K

0.0592	787.18	1154.8	0.0035	4.9
0.1025	787.03	1155.2	0.0020	2.9
0.1192	787.84	1155.5	0.0018	2.5
0.3412	785.14	1157	0.0007	0.9
0.5671	790.68	1158.3	0.0004	0.6
0.7874	790.12	1160.1	0.0003	0.4
1.0140	792.22	1161.9	0.0003	0.3
1.2380	792.84	1163.6	0.0002	0.3
1.4665	793.50	1165.5	0.0002	0.3
1.6901	795.18	1167.2	0.0002	0.2

T = 308.15 K

0.0592	782.80	1138.9	0.0036	4.8
0.1025	782.65	1139.3	0.0021	2.8

0.1192	783.46	1139.6	0.0018	2.4
0.3412	780.73	1142.1	0.0007	0.9
0.5671	786.23	1143.9	0.0004	0.5
0.7874	785.68	1145.9	0.0004	0.4
1.0140	787.74	1148.2	0.0003	0.3
1.2380	788.35	1150.1	0.0003	0.3
1.4665	789.00	1152.2	0.0002	0.2
1.6901	790.65	1154.8	0.0002	0.2

Methyl acetate + alcoholic solution of 0.0002 mol.kg^{-1} 2EQDPB

T = 293.15 K

0.0569	794.79	1173.2	0.0034	5.7
0.1018	802.35	1173.3	0.0018	3.0
0.1160	795.44	1173.4	0.0017	2.8
0.3410	797.51	1174	0.0006	1.0
0.5681	798.70	1175.8	0.0004	0.6
0.7894	800.44	1178.6	0.0003	0.5
1.0124	801.44	1181.6	0.0003	0.4
1.2385	802.18	1187.8	0.0002	0.3
1.4649	803.62	1191.9	0.0002	0.3
1.6902	804.22	1196.6	0.0002	0.2

T = 298.15 K

0.0569	790.51	1159.6	0.0035	5.6
0.1018	798.05	1159.8	0.0019	3.0
0.1160	791.15	1160.1	0.0018	2.8
0.3410	793.18	1160.6	0.0006	1.0
0.5681	794.36	1162.9	0.0004	0.6
0.7894	796.07	1165.6	0.0003	0.4
1.0124	797.05	1168.8	0.0003	0.4
1.2385	797.80	1173.1	0.0002	0.3
1.4649	799.19	1176.8	0.0002	0.3
1.6902	799.77	1180.8	0.0002	0.2

T = 303.15 K

0.0569	786.17	1140.6	0.0036	5.7
0.1018	793.69	1140.8	0.0019	3.0
0.1160	786.81	1141.2	0.0018	2.8
0.3410	788.81	1142.6	0.0007	1.0
0.5681	789.97	1144.2	0.0004	0.6
0.7894	791.63	1146.8	0.0003	0.5
1.0124	792.60	1149.2	0.0003	0.4
1.2385	793.36	1152.6	0.0002	0.3
1.4649	794.70	1155.6	0.0002	0.3
1.6902	795.25	1162.2	0.0002	0.2

T = 308.15K

0.0569	781.81	1118.5	0.0037	5.9
0.1018	789.29	1119.8	0.0020	3.0

0.1160	782.44	1120.1	0.0019	2.9
0.3410	784.40	1121.6	0.0007	1.0
0.5681	785.54	1123.4	0.0004	0.6
0.7894	787.16	1126.5	0.0003	0.5
1.0124	788.10	1130.2	0.0003	0.4
1.2385	788.87	1135.2	0.0003	0.3
1.4649	790.16	1138.6	0.0002	0.3
1.6902	790.70	1143.4	0.0002	0.2
	Methyl acetate + alcoholic solution of 0.0004 mol.kg^{-1} [4MQDB			
		T = 293.15 K		
0.0210	791.50	1198.6	0.0092	1.4
0.0691	791.90	1197.4	0.0029	0.4
0.1043	792.10	1196.2	0.0019	0.3
0.1404	792.10	1195.2	0.0015	0.2
0.1750	792.90	1194.5	0.0012	0.2
0.2091	793.00	1193.6	0.0010	0.1
0.5895	794.10	1186.2	0.0004	0.1
0.9653	795.90	1180	0.0003	0.0
1.3551	797.70	1174.5	0.0002	0.0
1.7300	800.40	1170.5	0.0002	0.0
		T = 298.15 K		
0.0210	787.20	1176.8	0.0096	1.4
0.0691	787.60	1175.2	0.0030	0.4
0.1043	787.70	1174.4	0.0020	0.3
0.1404	787.70	1173.1	0.0015	0.2
0.1750	788.60	1172.1	0.0012	0.2
0.2091	788.60	1171.4	0.0010	0.2
0.5895	789.80	1164.7	0.0004	0.1
0.9653	791.50	1159.8	0.0003	0.0
1.3551	793.30	1155.5	0.0002	0.0
1.7300	795.90	1153.2	0.0002	0.0
		T = 303.15 K		
0.0210	782.90	1162	0.0099	1.4
0.0691	783.20	1160.8	0.0031	0.4
0.1043	788.30	1159.8	0.0020	0.3
0.1404	783.40	1158.7	0.0016	0.2
0.1750	784.30	1157.8	0.0013	0.2
0.2091	784.30	1156.8	0.0011	0.1
0.5895	785.40	1148.8	0.0004	0.1
0.9653	787.10	1144.1	0.0003	0.0
1.3551	788.80	1139.1	0.0002	0.0
1.7300	791.40	1135.1	0.0002	0.0
		T = 308.15 K		
0.0210	778.50	1143.6	0.0103	1.4
0.0691	778.90	1142.1	0.0032	0.4
0.1043	779.00	1140.7	0.0021	0.3
0.1404	779.10	1139.9	0.0016	0.2

0.1750	779.90	1140.1	0.0013	0.2
0.2091	780.00	1138.5	0.0011	0.1
0.5895	781.00	1131	0.0004	0.1
0.9653	782.70	1126.6	0.0003	0.0
1.3551	784.40	1122.1	0.0002	0.0
1.7300	787.00	1119.1	0.0002	0.0

The experimental values given in **Table 4.3.1** of density(ρ) and sound velocity (u) for methyl acetate in 0.0005, 0.0003, 0.0002, 0.0004 mol.kg^{-1} alcoholic solution of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB, respectively against the molality of methyl acetate at different temperatures have been plotted in **Figs.4.3.1 (a-d) and 4.3.2 (a-d).**

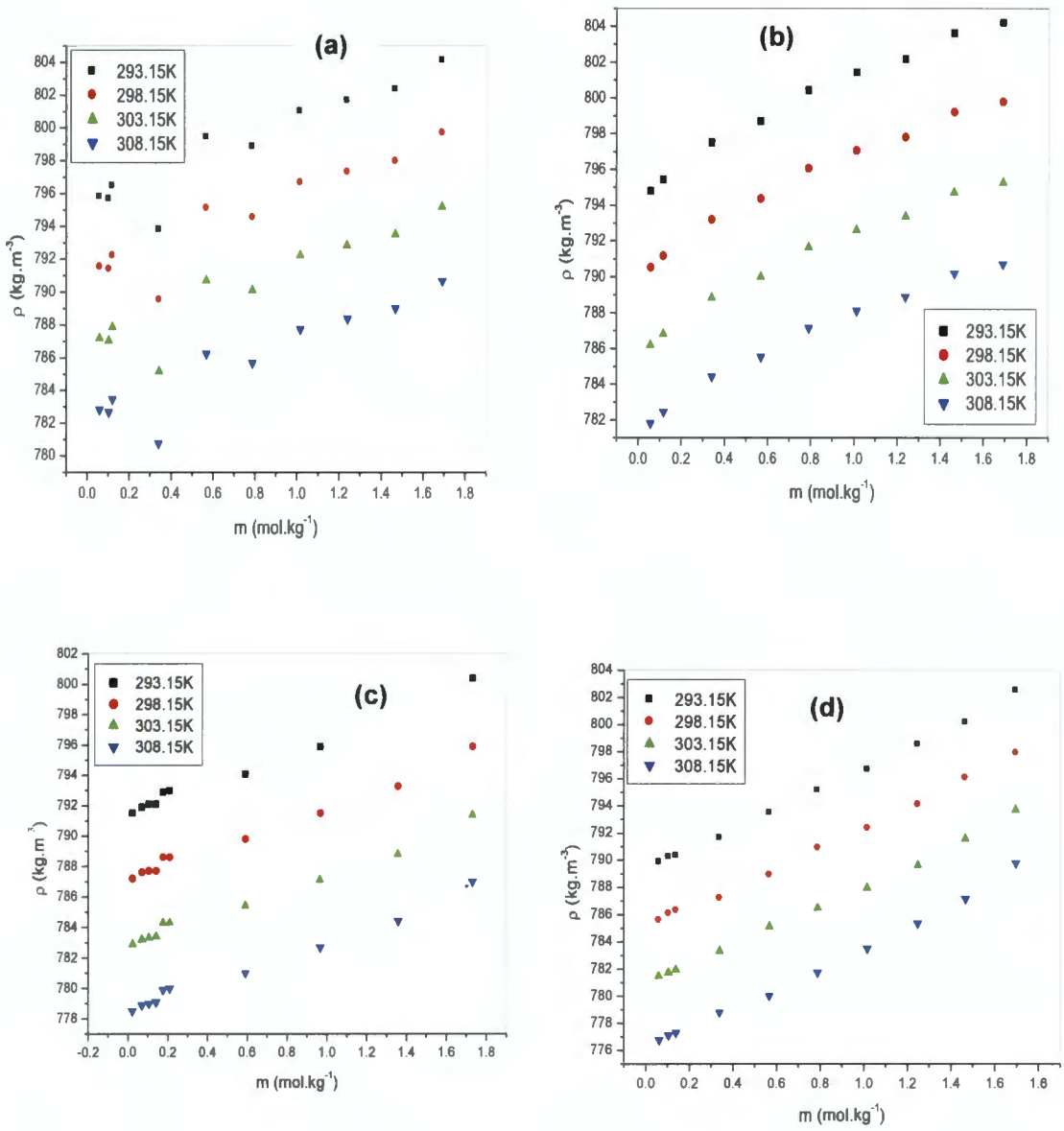


Fig. 4.3.1. Density (ρ), for the mixture of methyl acetate in alcoholic solution of (a) 2PQDE, (b) 4MQDPB, (c) 2EQDPB, (d) 4MQDB at 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

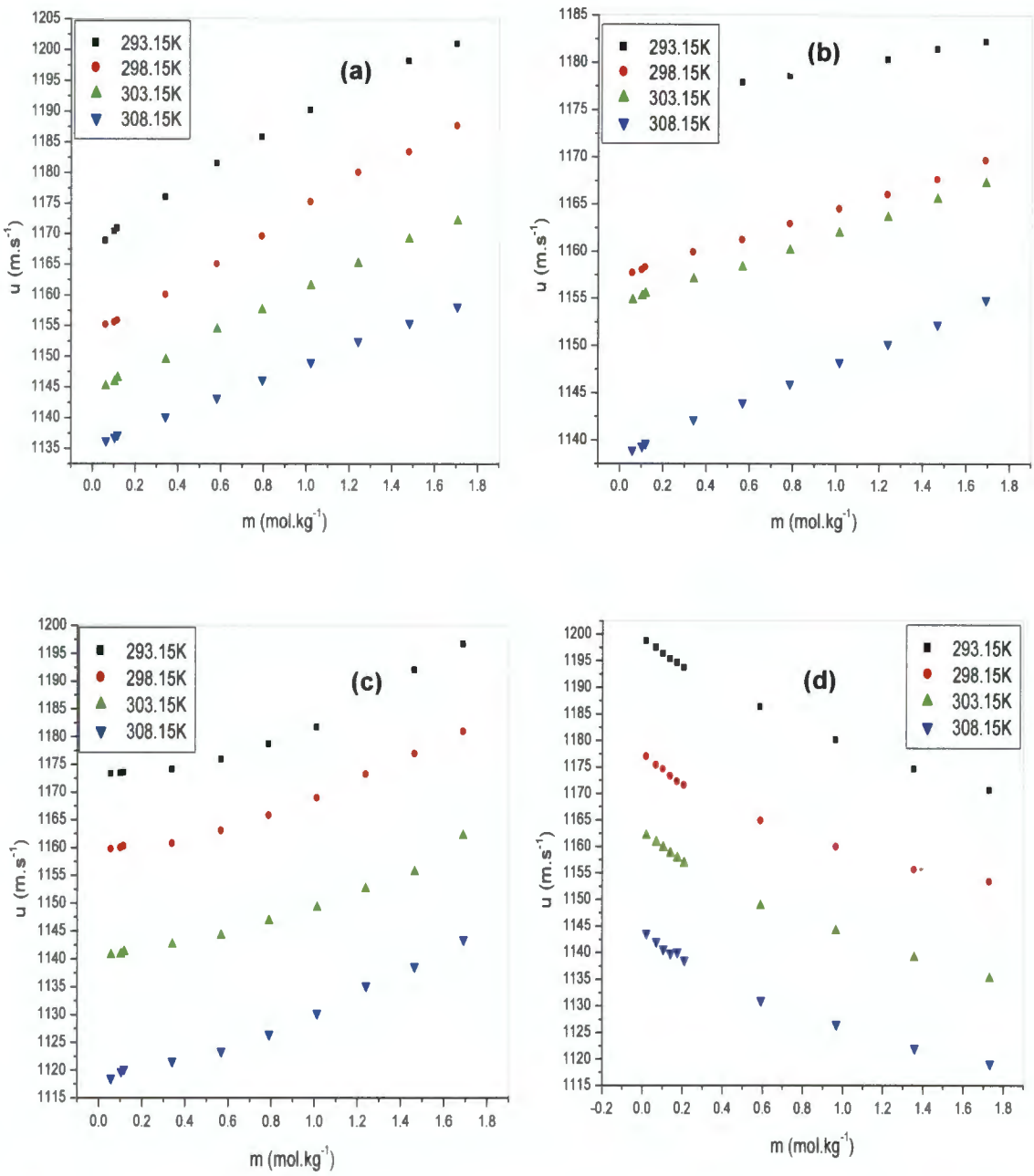


Fig. 4.3.2. Sound velocity (u), for the mixture of methyl acetate in alcoholic solution of (a) 2PQDE, (b) 4MQDPB, (c) 2EQDPB, (d) 4MQDB at T= 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

It can be seen from the **Figs 4.3.1 (a-d) and 4.3.2 (a-d),** that density and sound velocity increase with an increase in concentration and decreases with increase in temperature for all the systems except for the system 4MQDB, where the sound velocity values decrease with both cocentration and temperature. Density and sound velocity values are higher at lower cocentration for a specified temperature for all the binary systems. A similar trend was also observed in 1-ethyl-3-methylimidazolium ethyl sulphate system. The increasing values of density suggest the presence of strong intermolecular attraction such as solute-solvent attraction. An increase in concentration makes the solute and solvent molecules have closer approach and makes a strong association between solute and solvent molecules. This leads to decrease in the volume and an increase in the density of the solution. It is also observed that based on the structure and property of solute, the sound velocity values increase or decrease [163]. The decrease in sound velocity indicates that the interactions between solute and solvent is becoming less dominant. This is due to the replacement of strong intermolecular attraction between solvent molecules by weaker intermolecular interactions. This indicates that the solvent-solvent interaction is replaced by solute-solvent interaction.Thus, methyl acetate (solute) which is used in the Group III compounds decreases the values of sound velocity and therefore it acts as a structure breaker.

The values given in **Table 4.3.1** of V_φ and k_φ for methyl acetate in 0.0005, 0.0003, 0.0002, 0.0004 mol.kg^{-1} alcoholic solution of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB, respectively against the molality of methyl acetate at different temperatures have also been plotted in **Figs. 4.3.3 (a-d) and 4.3.4 (a-d).**

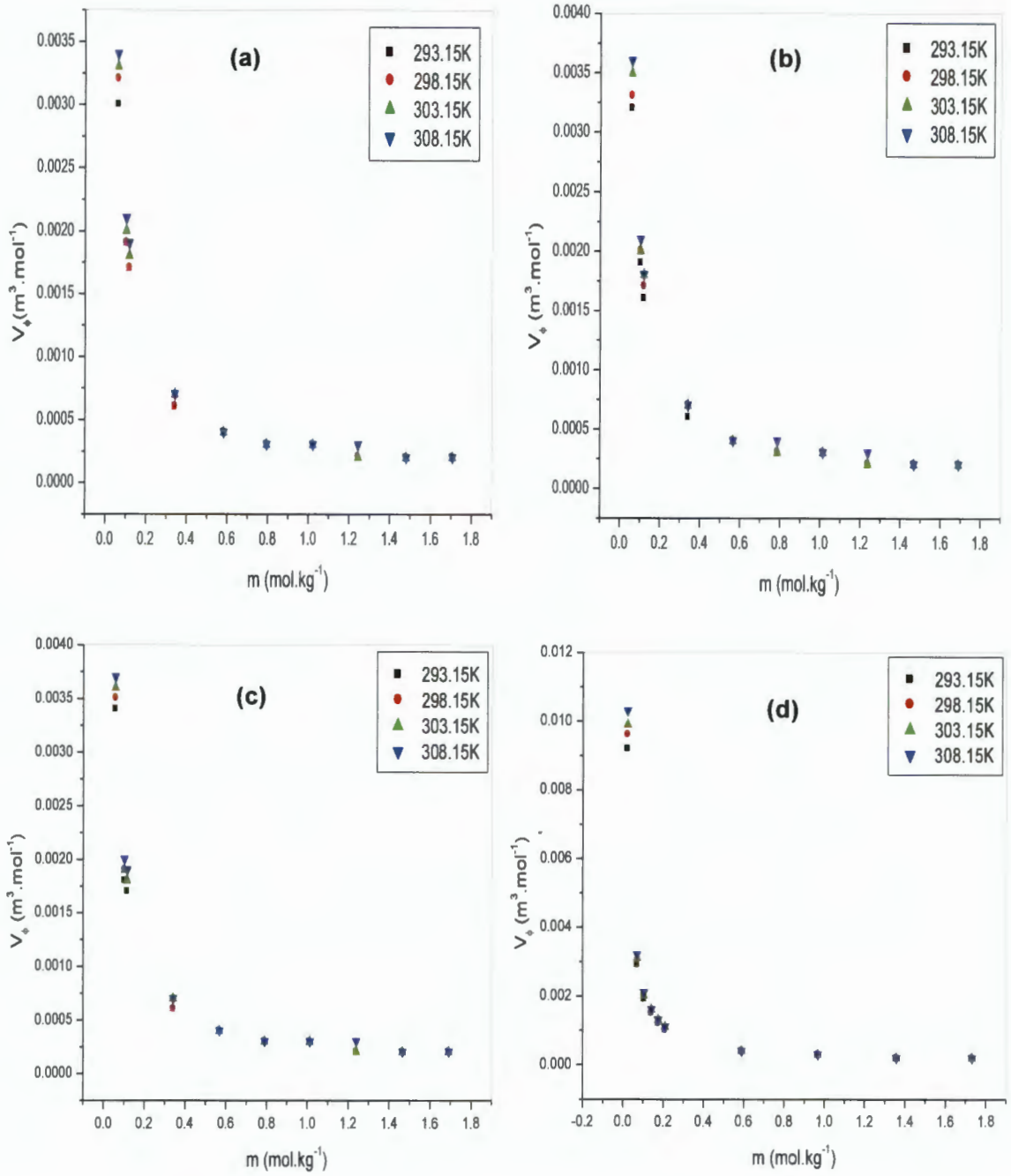


Fig. 4.3.3. Apparent molar volume, Vφ, for the mixture of methyl acetate in alcoholic solution of (a) 2PQDE, (b) 4MQDPB, (c) 2EQDPB, (d) 4MQDB at 293.15 K (■), T= 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

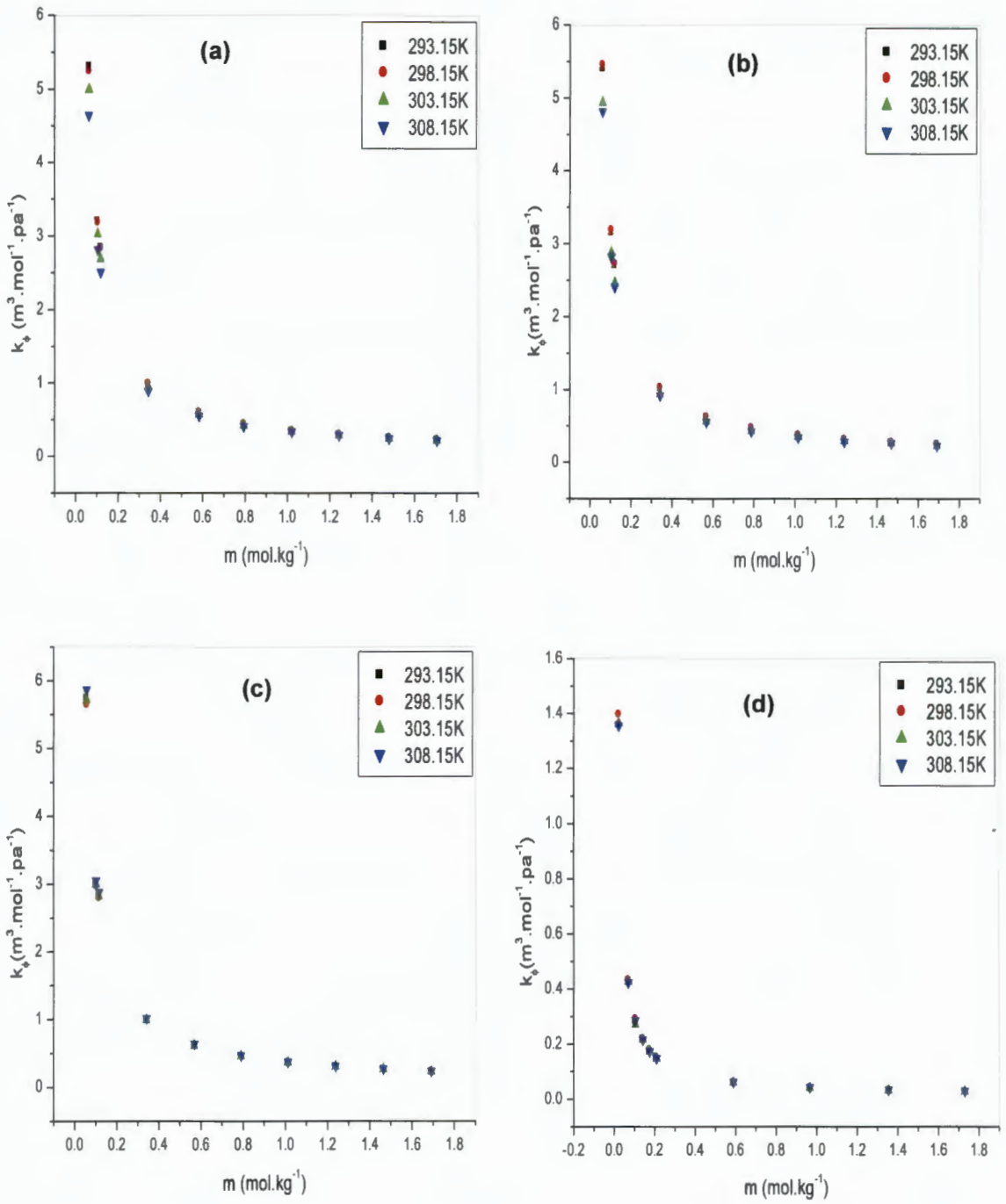


Fig. 4.3.4. Apparent molar adiabatic compressibility, kφ, for the mixture of methyl acetate in alcoholic solution of (a) 2PQDE, (b) 4MQDPB, (c) 2EQDPB, (d) 4MQDB at T= 293.15 K (■), 298.15 K (●), 303.15 K (▲) and 308.15 K (▼).

From the **Figs. 4.3.3 (a-e) and 4.3.4 (a-e),** it can be observed that the apparent molar volume (V_φ) decreased with increase in concentration and increases with increase in temperature while the apparent molar adiabatic compressibility (K_φ) values decreased with increase in concentration and temperature.The positive values of V_φ for all the binary system indicate strong solute-solvent interactions. These interactions are weakened with increasing concentration at a particular temperature. The V_φ values are low at higher concentration. Decreasing V_φ with increasing molality have also been observed in group II compounds.

The positive K_φ values are attributed to the weak solute-solvent interactions due to solvation of solute [166], and also indicates that the methyl acetate rich region is more compressable as compared to the bulk solution.

4.3.3 Apparent molar quantities at infinite dilution

The eqns (4.3 and 4.4) were used to calculate the apparent molar quantities at infinite dilution and the values have been presented in **Table 4.3.2 and 4.3.3.** The limiting apparent molar volume (V_φ^0), is the limiting volume that a substance occupies in one mole of other substance.

Table 4.3.2 Limiting apparent molar volumes (V_φ^0) and fitting parameters S_V and B_V of methyl acetate (solute) in alcoholic solution of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB at T= (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 MPa.

T (K)	V_φ^0 ($m^3.mol^{-1}$)	S_V ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2}$)	B_V ($m^3 \cdot mol^{-2} \cdot kg$)	σ
Methyl acetate + alcoholic solution of 0.0005 mol.kg^{-1} 2PQDE				
293.15	0.003	-0.008	0.003	0.0003
298.15	0.004	-0.009	0.004	0.0003
303.15	0.005	-0.010	0.005	0.0003
308.15	0.006	-0.011	0.006	0.0003
Methyl acetate + alcoholic solution of 0.0003 mol·kg^{-1} 4MQDPB				
293.15	0.004	-0.009	0.004	0.0003
298.15	0.005	-0.010	0.005	0.0003
303.15	0.006	-0.011	0.006	0.0004
308.15	0.007	-0.012	0.007	0.0004
Methyl acetate + alcoholic solution of 0.0002 mol·kg^{-1} 2EQDPB				
293.15	0.005	-0.010	0.005	0.0004
298.15	0.006	-0.011	0.006	0.0004
303.15	0.007	-0.012	0.007	0.0004
308.15	0.008	-0.013	0.008	0.0004
Methyl acetate + alcoholic solution of 0.0004 mol·kg^{-1} 4MQDB				
293.15	0.010	-0.024	0.014	0.0016
298.15	0.011	-0.025	0.015	0.0017
303.15	0.012	-0.026	0.016	0.0017
308.15	0.013	-0.027	0.017	0.0018

V_φ^0 is the limiting apparent molar volume which is also equal to the partial molar voume. S_v is the experimental slope which is also considered to be a volumetric pairwise interaction coefficient [184]. The positive sign of V_φ^0 reflects the nature of solute-solvent interaction and the magnitude of *S*v related to solute-solute interaction. The limiting apparent molar volume based upon the molecular shape, size, polarity interactions and structural effects of different components. In group III compounds, the values of V_φ^0 are positive for all the binary systems at all temperatures and increses with an increase in temperature. This indicates the presence of strong solute–solvent interactions and these interactions increases with increase in temperature which is opposite to Group I compounds. The *S*v values are negative for all the systems and decreases with an increase in temperature for all the systems which is also opposite to Group I compounds. The (solute-solute) interactions are stronger for 2PQDE than for 4MQDPB than for 2EQDPB than for 4MQDB. The solute-solute interactions decrease with an increase in temperature for all the systems in Group III. The *B*v values are positive for all the systems. The B_v value increases with an increase in temperature for all the systems. The positive B_v values indicate decrease in solute-solute interactions for all the systems which is also opposite to Group I set of compounds.

Limiting apparent molar adiabatic compressibility, k_φ^0, were calculated using equation (4.3 and 4.4) given in Group I and the values of k_φ^0, S_k and B_k are presented in **Table 4.3.3.**

Table 4.3.3 Limiting apparent molar adiabatic compressibility, k_{φ}^{0}, and fitting parameters S_k and B_k, of methyl acetate (solute) in alcoholic solution of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB at T= (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 MPa

T (K)	k_{φ}^{0} ($m^3.mol^{-1}.Pa^{-1}$)	S_k ($m^3 \cdot mol^{-3/2} \cdot kg^{1/2} pa^{-1}$)	B_k ($m^3 \cdot mol^{-2} \cdot kg.\ pa^{-1}$)	σ
Methyl acetate + alcoholic solution of 0.0005 mol.kg^{-1} 2PQDE				
293.15	7.6	-14.7	7.1	0.5
298.15	7.5	-14.4	7.0	0.5
303.15	7.1	-13.7	6.7	0.5
308.15	6.6	-12.7	6.2	0.5
Methyl acetate + alcoholic solution of 0.0003 mol·kg^{-1} 4MQDPB				
293.15	7.6	-14.7	7.3	0.5
298.15	7.5	-14.6	7.2	0.6
303.15	6.9	-13.4	6.6	0.5
308.15	6.7	-13.1	6.4	0.5
Methyl acetate + alcoholic solution of 0.0002 mol·kg^{-1} 2EQDPB				
293.15	7.8	-15.3	7.5	0.6
298.15	7.7	-15.0	7.4	0.6
303.15	7.6	-14.9	7.3	0.6
308.15	7.5	-14.8	7.2	0.7
Methyl acetate + alcoholic solution of 0.0004 mol·kg^{-1} 4MQDB				
293.15	1.5	-3.7	2.1	0.2
298.15	1.4	-3.6	2.0	0.2
303.15	1.3	-3.5	1.9	0.2
308.15	1.2	-3.4	1.8	0.2

The positive k_{φ}^{0} values of all the systems may be interpreted in terms of an increase in the compressibility of the solution compared to the solvent 2PQDE, 4MQDPB, 2EQDPB and 4MQDB. This also indicates the presence of week solute–solvent interactions. Positive k_{φ}^{0}, for 2PQDE, 4MQDPB, 2EQDPB and 4MQDB systems are due to the fact that solvent intrinsic compressibility is greater than the penetration effect which is similar to Group I compounds. These indicate that the 2PQDE, 4MQDPB, 2EQDPB or 4MQDB molecules being released from methyl acetate should present lesser resistance to compression than the bulk solvent. The k_{φ}^{0} values decreases with an increase of temperature. The S_k values are negative and increases with temperatures while the B_k values are positive and decreases with temperatures. The empirical parameters S_k and B_k have the same meaning as S_v and B_v.

4.3.4. Thermal expansion coefficients (α_p)

The isobaric thermal expansion coefficient, α_p of the solutes can be calculated using the apparent molar volume and apparent molar expansibility at infinite dilution data using eqn (4.5). The values of the isobaric thermal expansion coefficients, α_p, of all the four binary systems are given in **Table 4.3.4**

Table 4.3.4 The limiting apparent molar expansibility, E_{φ}^{0} and isobaric thermal expansion coefficients α_p.

Solute	Solvent	E_{φ}^{0} ($m^3 \cdot mol^{-1} \cdot K^{-1}$)			
		$T = 293.15$ K	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K
Methyl acetate	2PQDE	0.000207	0.000108	0.000106	0.000093
Methyl acetate	4MQDPB	0.000205	0.000107	0.000105	0.000094
Methyl acetate	2EQDPB	0.000089	0.000086	0.000084	0.000078
Methyl acetate	4MQDB	0.000087	0.000083	0.000080	0.000075
		α_p (K^{-1})			
Methyl acetate	2PQDE	0.0519	0.0215	0.0160	0.0186
Methyl acetate	4MQDPB	0.0518	0.0214	0.0140	0.0186
Methyl acetate	2EQDPB	0.0089	0.0015	0.0013	0.0010
Methyl acetate	4MQDB	0.0087	0.0018	0.0016	0.014

It can be observed from the **Table 4.3.4,** that the values of α_p are small and decreases with an increase in temperature for all systems.

4.3.5. Limiting apparent molar expansivities

The limiting apparent molar expansibility E_{φ}^{0} can be obtained by differentiating eqn. (4.6) with respect to temperature. The E_{φ}^{0} values for each binary system are also presented in **Table 4.3.4** and the values provide important information about the (solute-solvent) interactions [173].

Table 4.3.4 shows that at each temperature E_{φ}^{0} values are positive for all the systems and decreases with an increase in temperature. The decrease in the E_{φ}^{0} values with temperature indicate decrease in thermal agitation, resulting in solvent molecules being released from methyl acetate, thereby increasing the solution volume to a greater extent than for the solvent

The positive values of E_{φ}^{0} indicate the presence of stong solute-solvent interactions in all the solutions investigated. The trend for group III compunds is opposite to Group I compunds.

The values of $\left(\partial^2 V_{\varphi}^{0} / \partial T^2\right)_P$ are -2x10^{-5}, -2x10^{-5}, 0, 2x10^{-5} for methyl acetate in alcoholic solution of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB, respectively which suggest that the solute methyl acetate acts as a structure maker for 2EQDPB and 4MQDB and structure breaker for 2PQDE and 4MQDPB in the solutions.

4.3.6. Partial molar quantities of transfer

The partial molar volumes of transfer, ΔV_{φ}^{0}, and partial molar adiabatic compressibility of transfer, ΔK_{φ}^{0}, from water to alcoholic solution of quinoxaline derivatives were calculated using the equation (4.9) and their corresponding values are presented in **Table 4.3.5.**

Table 4.3.5 Partial molar volume of transfer, ΔV_{φ}^{0}, and partial molar adiabatic compressibility of transfer, Δk_{φ}^{0}, of methyl acetate (solute) in alcoholic solution of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB at (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 MPa.

T (K)	ΔV_{φ}^{0} ($m^3 \cdot mol^{-1}$)	Δk_{φ}^{0} ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)
Methyl acetate + alcoholic solution of 0.0005 mol.kg^{-1} 2PQDE		
293.15	-0.0004	-0.9184
298.15	-0.0002	-1.0728
303.15	0.0001	-1.4489
308.15	0.0003	-2.4790
Methyl acetate + alcoholic solution of 0.0003 mol·kg^{-1} 4MQDPB		
293.15	-0.0002	-0.9727
298.15	-0.0001	-0.9829
303.15	0.0002	-1.6861
308.15	0.0004	-2.3819
Methyl acetate + alcoholic solution of 0.0002 mol·kg^{-1} 2EQDPB		
293.15	-0.0000	-0.7165
298.15	0.0001	-0.9148
303.15	0.0002	-0.9338
308.15	0.0005	-1.1708
Methyl acetate + alcoholic solution of 0.0004 mol·kg^{-1} 4MQDB		
293.15	0.0049	-7.1097
298.15	0.0053	-7.1123
303.15	0.0056	-7.1677
308.15	0.0061	-7.6961

The **Table 4.3.5** shows that ΔV_{φ}^{0} values are small with both positive and negative and increases with increase in temperature for all the systems. The negative values of ΔV_{φ}^{0} of methyl acetate in alcoholic solutions of 2PQDE, 4MQDPB, 2EQDPB and 4MQDB may be attributed to the decrease in the solute-solvent interactions while positive values attributed to the increase in the solute-solvent interactions at infinite dilution [178]. The ΔK_{φ}^{0} values are negative for all the systems and decreases with increase in temperature which is opposite to Group I compunds. This may be ascribed to increasing of electrostricted ethanol molecules around 2PQDE, 4MQDPB, 2EQDPB and 4MQDB [179].

CHAPTER 5

CONCLUSION

In the present work, new data of density and sound velocity of methyl acetate in aqueous solution of quinoxaline derivatives namely: MQDPMS, AQDPMS, 2PQDPMS, 3PQDPMS (Group I) and alcoholic solution of quinoxaline derivatives namely: BQDB, 3MQDPP, 3PQDB, 4CQDPP (Group II), 2PQDE, 4MQDPB, 2EQDPB and 4MQDB (Group III), have been generated and reported in the temperature range (293.15 to 308.15) K and at pressure p = 0.1 MPa. The apparent molar volume (V_φ), and apparent molar adiabatic compressibility (k_φ), for the mixtures were calculated using these data. The limiting apparent molar volumes (V_φ^0), limiting apparent molar volumes of transfer (ΔV_φ^0), limiting apparent molar adiabatic compressibility (k_φ^0), and limiting apparent molar adiabatic compressibility (Δk_φ^0), of transfer were evaluated by fitting Redlich-Mayer type equation and reasonable correlations were achieved. Furthermore, the limiting apparent molar expansibility, (E_φ^0), and the Hepler's constant $\left(\partial^2 V_\varphi^0 / \partial T^2\right)_p$ values, were also evaluated to support the conclusions drawn from volumetric and acoustic studies.

These results have been interpreted in terms of effect of temperature, concentration as well as structural variation of quinoxaline derivatives on interactions such as solute–solute, solute–solvent and solvent–solvent which exist in the mixtures. The results obtained from the work shows that the values of density, (ρ) are found to increase with an increase in concentration and decreased with temperature for all three Groups I, II and III set of quinoxaline derivatives while the values of sound velocity (u) exhibited an increasing trend with both temperature and concentration for Group I compound and decreased with both concentration and temperature for Groups II and III set of quinoxaline derivatives. The increase in the values of density is due to presence of strong intermolecular attraction such as solute-solvent attraction. An increase in

concentration allows for a closer approach of solvent and solute molecules, and stronger association between solute and solvent molecules. The decrease in sound velocity indicates that the interactions between solute and solvent is becoming less dominant. This is due to the replacement of strong intermolecular attraction between solvent molecules by weaker intermolecular interactions. This indicates that the solvent-solvent interaction is replaced by solute-solvent interaction.

The apparent molar volume decreased with an increase in concentration for Groups II and III which is opposite to Group I. The apparent molar volumes are negative, but only few are positive at higher concentration for Group I whereas all are positive for Groups II and III. The negative values suggests that the overall structural order is reduced in solution whereas positive values suggests that the overall structural order is enhanced in solution. The apparent molar adiabatic compressibility ($k\varphi$) values are positive but decreased with increase in concentration of solute at a fixed temperature for all the systems for all Groups I, II and III. The positive $k\varphi$ values indicate that methyl acetate rich region is more compressible as compared with bulk solution. The positive $k\varphi$ values are attributed to the weak interactions between the solute and solvent.

The values of V_φ^0 are positive for Groups II and III whereas negative for Group I at all temperatures suggesting that there is presence of strong solute–solvent interactions for Group II and III and week solute-solvent interactions for Group I set of quinoxaline derivatives. The S_v values are negative for Group II and III at each temperature which is also opposite to Group I compounds. The B_v values are positive for Group II and III whereas negative for Group I. The k_φ^0 values are positive for all Groups and decreased with an increase of temperature for Group I and III except Group II where there is increase with temperature. This indicates the presence of weak solute-solvent interactions.

The E_{φ}^{0} values are positive for Groups II and III except Group I where there are negative; increased with an increase in temperature for Groups I and II but decreased for Group III. The decrease in the E_{φ}^{0} values with temperature indicate decrease in thermal agitation, resulting in solvent molecules being released from methyl acetate, thereby increasing the solution volume to a greater extent than for the solvent. The positive values of E_{φ}^{0} indicate the presence of strong solute-solvent interactions. The solute methyl acetate acts as a mixed type such as structure maker and breaker in the solutions for Group I, II and III. ΔV_{φ}^{0} values are negative for Groups I and II but both positive and negative for Group III. The negative values of ΔV_{φ}^{0} may be attributed to the decrease in the solute-solvent interactions while positive values may be attributed to the increase in the solute-solvent interactions at infinite dilution. The ΔK_{φ}^{0} values are negative for all the systems and decreased with increase in temperature for Groups II and III which is opposite to Group I. Thus, the results from these studies can be utilized in flow assurance and oil recovery, design of separation processes, solvent selection and emission, estimation of the distribution of chemicals in various ecosystems. Material energy balance calculations for any process require the knowledge of thermophysical properties including density and heat capacity. The latter two properties are important process parameters for effective design of esterification reactions on an industrial scale. In the present work, direct density measurements are reported whereas heat capacities can be calculated from the reported speed of sound data. It is a well-known fact that reliable experimental data ensure a higher degree of accuracy than correlations used to estimate unknown properties. Thus, the results from these studies can be utilized in flow assurance and oil recovery, design of separation processes, solvent selection and emission, estimation of the distribution of chemicals on an industrial scale.

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APPENDIX 1

Results for (ethanol + methyl acetate) system

TABLE 1A

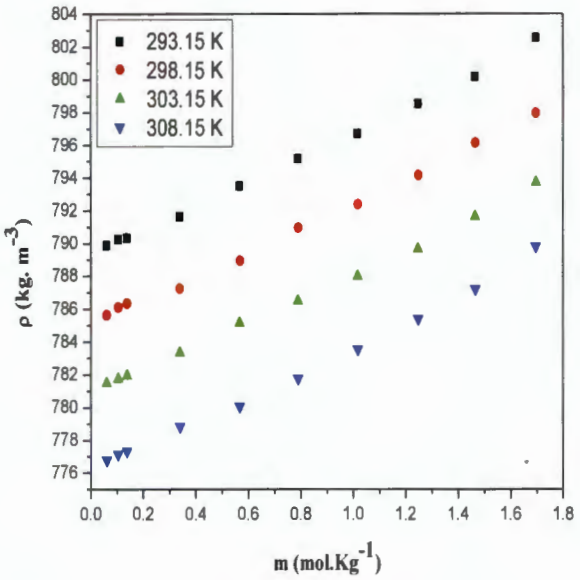
The density (ρ), sound velocity (u), apparent molar volume (V_φ), and apparent molar adiabatic compressibility (k_φ) of ethanol + methyl acetate system T= (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 MPa.

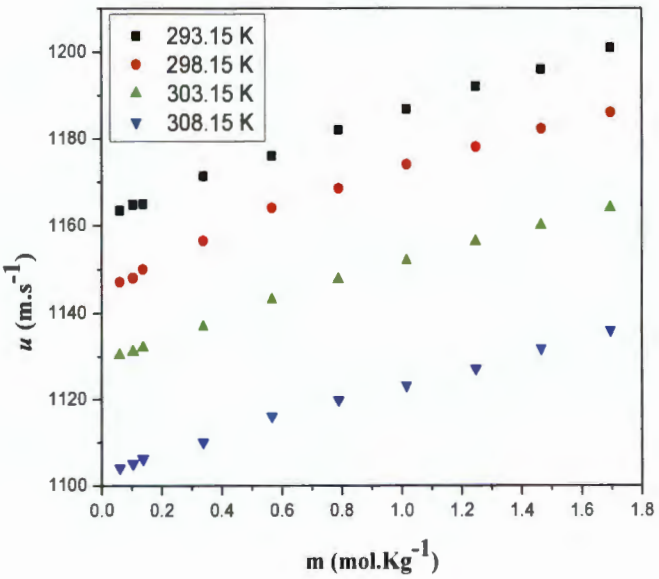
m (mol·kg^{-1})	ρ (kg·m^{-3})	u (m·s^{-1})	V_φ (m^3·mol^{-1})	k_φ (m^3·mol^{-1}·Pa^{-1})
		Ethanol + methyl acetate		
T=293.15 K				
0.0599	789.88	1163.5	0.0033	6.0278
0.1037	790.24	1164.8	0.0020	3.4855
0.1379	790.33	1165.0	0.0015	2.6381
0.3385	791.65	1171.4	0.0007	1.0758
0.5662	793.52	1176.0	0.0004	0.6510
0.7884	795.18	1182.0	0.0003	0.4695
1.0159	796.71	1186.8	0.0003	0.3689
1.2463	798.55	1192.0	0.0002	0.3030
1.4641	800.19	1196.0	0.0002	0.2611
1.6949	802.55	1200.9	0.0002	0.2265
***T*=298.15 K**				
0.0599	785.59	1147.0	0.0033	6.0540
0.1037	786.07	1148.0	0.0020	3.5028
0.1379	786.30	1149.9	0.0015	2.6220
0.3385	787.22	1156.4	0.0007	1.0717
0.5662	788.91	1164.0	0.0004	0.6383

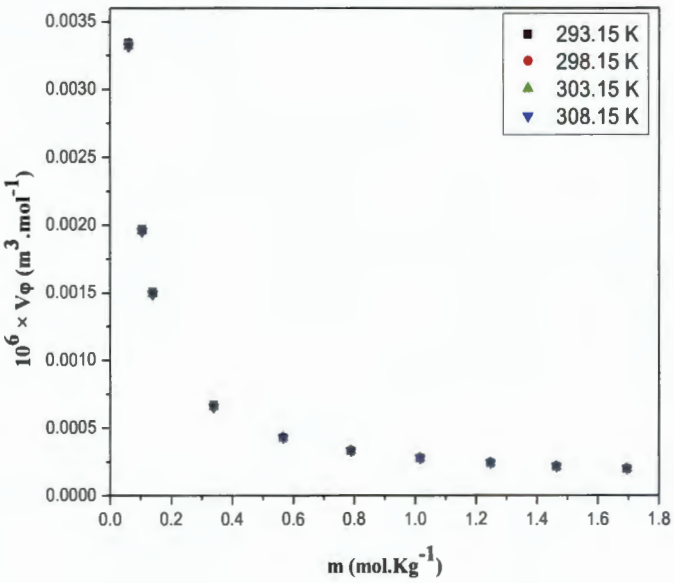
0.7884	790.92	1168.5	0.0003	0.4629
1.0159	792.36	1174.0	0.0003	0.3626
1.2463	794.12	1178.0	0.0002	0.3001
1.4641	796.11	1182.2	0.0002	0.2576
1.6949	797.93	1186.0	0.0002	0.2257
***T*=303.15 K**				
0.0599	781.50	1130.3	0.0033	6.0671
0.1037	781.73	1131.0	0.0020	3.5247
0.1379	781.94	1132.0	0.0015	2.6528
0.3385	783.34	1136.8	0.0007	1.0904
0.5662	785.13	1143.0	0.0004	0.6538
0.7884	786.48	1147.5	0.0003	0.4768
1.0159	787.97	1152.0	0.0003	0.3753
1.2463	789.63	1156.3	0.0002	0.3103
1.4641	791.60	1160.0	0.0002	0.2670
1.6949	793.74	1164.0	0.0002	0.2330
***T*=308.15 K**				
0.0599	776.77	1104.0	0.0033	6.4474
0.1037	777.12	1105.0	0.0019	3.7339
0.1379	777.31	1106.1	0.0015	2.8085
0.3385	778.81	1110.0	0.0007	1.1591
0.5662	780.05	1116.0	0.0004	0.6986
0.7884	781.76	1119.7	0.0003	0.5099
1.0159	783.53	1123.1	0.0003	0.4028
1.2463	785.37	1127.0	0.0002	0.3329
1.4641	787.17	1131.7	0.0002	0.2851
1.6949	789.78	1136.0	0.0002	0.2472

FIGURE 1A

The density (ρ), sound velocity (u), apparent molar volume (V_φ), and apparent molar adiabatic compressibility (k_φ) of ethanol + methyl acetate system at 293.15, 298.15, 303.15 and 308.15 K and at pressure p = 0.1 MPa






293.15 K
298.15 K
303.15 K
308.15 K
$10^6 \times V\varphi$ ($m^3.mol^{-1}$)
m ($mol.Kg^{-1}$)

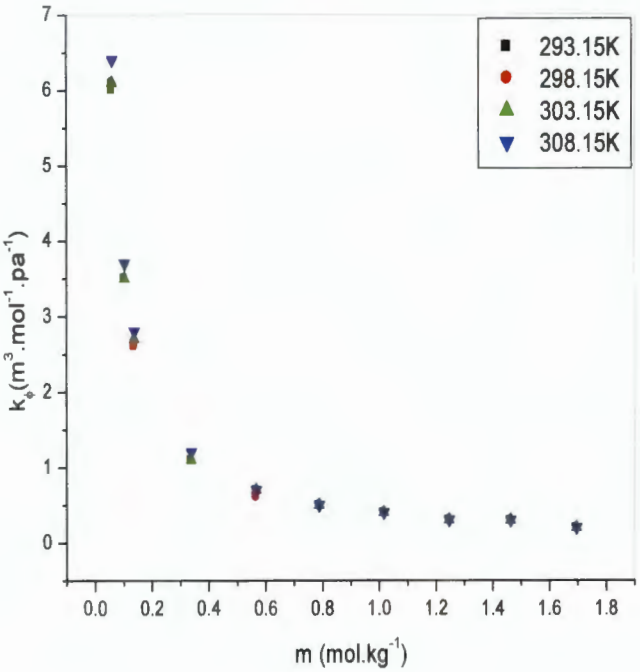

293.15K
298.15K
303.15K
308.15K
k_ϕ($m^3.mol^{-1}.pa^{-1}$)
m ($mol.kg^{-1}$)

TABLE 2A

The limiting apparent molar volume, V_{φ}^{0}, and apparent molar adiabatic compressibility, K_{φ}^{0} of ethanol + methyl acetate system at (293.15, 298.15, 303.15 and 308.15) K and at pressure p = 0.1 Mpa.

T (K)	V_{φ}^{0} ($m^3.mol^{-1}$)	K_{φ}^{0} ($m^3.mol^{-1}.pa^{-1}$)
293.15	0.005	8.5
298.15	0.005	8.6
303.15	0.005	8.6
308.15	0.005	9.1

APPENDIX 2

List of publications

[1] **R. Gnanapragasam**, I. Bahadur, E. E. Ebenso, "Interaction studies of methyl acetate in aqueous solutions of quinoxaline derivatives: Effect of temperature and concentration" **Journal of Molecular Liquids, 211 (2015) 567-576.**

[2] **R. Gnanapragasam**, I. Bahadur, E. E. Ebenso, Density, sound velocity and their derived properties of some selected quinoxaline derivatives in alcoholic solutions with methyl acetate at different temperatures. **Journal of Molecular Liquids (under review).**

[3] **R. Gnanapragasam**, I. Bahadur, E. E. Ebenso, Thermophysical approach to understand the nature of molecular interactions and structural factor between methyl acetate with alcoholic solution of quinoxaline derivatives. **Journal of Chemical Thermodynamics (under review).**

Conference presentation

[1] **R. Gnanapragasam**, I. Bahadur, E. E. Ebenso, Interaction studies of methyl acetate in aqueous solutions of quinoxaline derivatives: Effect of temperature and concentration" **New Frontiers in Chemistry- from Fundamentals to Applications.(NFCFA 2015), Date 18 and 19th December 2015, organished by Department of Chemistry, BITS Pilani KK Birla, Goa, India.**